SOME REACTIONS OF COBALT CARBONYL COMPLEXES IN SOLUTION

BY ALISON ELIZABETH LESLIE B.Sc., GRAD. R.S.C.

A THESIS SUBMITTED IN FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE UNIVERSITY OF GLASGOW

NOVEMBER 1981

The jewel's cost is labour. The diamond in the mine
Needs men to go and find it, and men to sit and shine.
Not in itself lies value. The ores that fill the earth
Are barren things and useless till man has given them worth.
The pioneer must find them; the scientist must dream;
And some must back adventure, though great the risk may seem,
Then some must tend the boiler, and some must drive the dray;
But which is more important not one of us can say.

TABLE OF CONTENTS

Acknowledgements

Declaration

Abstract

Abbreviations

CHAPTER 1 - INTRODUCTION

1. Cobalt 1

2. Metal Carbonyls 5

3. Cobalt Carbonyls 27

CHAPTER 2 - FORMATION OF TETRACARBONYL COBALTATE (-1)

1. Introduction 57

2. Halide Induced Disproportionation of $Co_2(CO)_8$ in T.H.F. and Its Reactions 90

3. Halide Induced Disproportionation of $Co_2(CO)_8$ in Diethyl Ether and Its Reactions 108

4. Valence Disproportionation in Hydrocarbon Solvents 120

5. Experimental 122

6. Discussion 141

CHAPTER 3 - FORMATION AND REACTIONS OF $[Co_3(CO)_{10}]^-$

1. Introduction 147

2. Formation of $[Co_3(CO)_{10}]^-$ as an intermediate in Disproportionation Reactions 157

3. Formation and Reactions of $[Co_3(CO)_{10}]^-$ using Alkali Metals in Diethyl Ether 159

4. Experimental 166

5. Discussion 174

CHAPTER 4 - MERCURY - COBALT CARBONYL COMPOUNDS

1. Introduction 185

2. Reactions of $Hg[Co(CO)_4]_2$ in Ethereal Solvents 194

3. Reactions of $Co_2(CO)_8$ with Sodium Amalgam or Mercury in Ethereal Solvents 204

4. Experimental 209

5. Discussion 221

CHAPTER 5 - TETRACOBALT DODECACARBONYL AND ITS REACTIONS

1. Introduction 226

2. Preparation and Reactions of $Co_4(CO)_{12}$ in Ethereal Solvents 238

3. Experimental 248

4. Discussion 257

CHAPTER 6 - MISCELLANEOUS

1. Kinetics of Disproportionation by n-Tetrabutyl Ammonium Iodide 259

Experimental 260

Discussion 262

2. Cobalt Dibromide in Ethereal Solvents 262

Experimental 268

Discussion 269

3. Tetraphenylphosphonium Tetracarbonylcobaltate (-1) 271

Experimental 283

Discussion 284

CHAPTER 7 - PERSPECTIVE 285

References.

Acknowledgements

Firstly I wish to record my grateful thanks to my supervisor, Dr. P.S. Braterman who not only suggested the line of research but rendered assistance and encouragement at all times.

Thanks are also due to members of staff and postgraduate students who not only helped but also put up with me for three years. In this category Prof. D.W.A. Sharp, Dr. R.J. Cross, Dr. M. Mercer and the organometallic research students rate special mention.

The valued technical assistance of Mrs. Freda Lawrie and Linda in recording Perkin Elmer 5080 infrared spectra is acknowledged; also Dr. D. Rycroft, for recording the n.m.r. spectra, Dr. R.D. Peacock for recording the Raman spectrum, and the microanalysis and glass-blowing departments. Much help was forthcoming from Mr. G. Saunders in his capacity as librarian especially in keeping me sane during the writing of this thesis.

Final words of praise are reserved for my family - for my mother who spent many an evening typing, to my sister for her aid in drawing diagrams and to my father for putting up with it all.

Declaration

Part of this work has been published as detailed below:

a) Note by P.S. Braterman, A.E. Leslie and B.S. Walker, J.C.S. Dalton (1980), 2318. This was concerned with $CoBr_2$ (etherates).

b) Strong interactions between $[Co(CO)_4]^-$ and Li^+ or Na^+ in diethyl ether by P.S. Braterman and A.E. Leslie, J. Organomet. Chem. 214, (1981), C45.

Abstract

The aim of this research was to further the knowledge and understanding of the reactions of dicobalt octacarbonyl. This subsequently has been split into four main areas.

Initially investigation into the formation of the anion tetracarbonyl cobaltate (-1), $[Co(CO)_4]^-$, using a range of halide salts and lithium salts as the disproportionating reagent, and in different solvents and atmospheres, was undertaken. An abortive attempt at studying the kinetics of this reaction was made.

On discovering the complexity of reaction when diethyl ether was the solvent, the next set of experiments were concerned with the reduction of $Co_2(CO)_8$ in ethereal solvents using sodium amalgam. This proved to be no less complicated, showing that an intermediate complex, $[Co_3(CO)_{10}]^-$, persisted in solution. In diethyl ether the not inconsiderable effect of the cation on $[Co(CO)_4]^-$ was demonstrated by the shift of i.r. absorption frequency, and the line shape, of the anion.

Further research into the interaction of mercury containing species and $Co_2(CO)_8$ provided a series of mercury - cobalt carbonyl anions, of the form $\{Hg[Co(CO)_4]_2X\}^-$ (X = Cl, Br or $Co(CO)_4$), being isolated as the $[M(\underline{o}phen)_3]^{2+}$ (M = Fe, Ni) derivatives. The ratio of the different species isolated in the solid form depended on the solvent used in the experiment and the metal ion in the phenanthroline derivative.

To elucidate the nature of certain mysterious species present in reactions of $Co_2(CO)_8$ with disproportionating reagents a series of experiments involving $Co_2(CO)_8$, $Co_4(CO)_{12}$ and $[Co(CO)_4]^-$ (in varying amounts) were conducted. Those involving $Co_2(CO)_8$ and $Co_4(CO)_{12}$ only showed the large effect on the i.r. spectrum (terminal carbonyl region) that trace amounts of one of the reactants can wield. Hence it was

deduced that the variation in i.r. spectra observed were not due to a new complex but due to the interactions of species already present in solution.

Finally two isolated pieces of research have been noted. The first involved preparation of $CoBr_2$ $(etherate)_x$ compounds in the solid form and studying the U.V. / visible spectrum, in both the solid and solution phases, to derive the coordination of Co^{2+}. The other item of work was the preparation and characterisation of $[Ph_4P]^+ [Co(CO)_4]^-$, a new solid form of the anion. The reactions of this compound were looked into in conjunction with other sections of the research.

Abbreviations

a) Units.

atm	atmosphere
^{o}C	degree Celsius
eV	electron volt
g	gram
h	Plank's constant (6.63×10^{-34} Joules)
hr	hour
l	litre
m	metre
M	molar (mole l^{-1})
min	minute
sec	second

b) Multipliers.

c	centi
k	kilo
m	milli
n	nano
μ	micro

c) Spectral.

cm^{-1}	wavenumber
m	medium
max	maximum
p.p.m.	parts per million
s	strong
sh	shoulder
vs	very strong
vw	very weak
w	weak
δ	chemical shift in p.p.m. downfield t.m.s. (in n.m.r.)
$\tilde{\nu}$	a stretching mode of vibration

d) General.

acac	acetylacetonate
Bu	butyl
c.f.	compare
concn.	concentration
cp	cyclopentadienyl
diglyme	diethyleneglycoldimethylether
D.M.E.	dimethyl ether
D.M.F.	dimethylformamide
D.M.S.O.	dimethylsulphoxide
E.A.N.	effective atom number (eighteen electron rule)
e.p.r.	electron paramagnetic resonance
e.s.r.	electron spin resonance
Et	ethyl
EtOH	ethanol

Fig.	figure
glyme	ethyleneglycoldimethylether
H.M.P.A.	hexamethylphosphoric triamide
H.O.M.O.	highest occupied molecular orbital
H.T.F.	high temperature form
i	iso
i.r.	infrared
$\log_{10}$	logarithm to the base 10
L.T.F.	low temperature form
L.U.M.O.	lowest unoccupied molecular orbital
Me	methyl
MeCN	acetonitrile
MeOH	methanol
2-M.T.H.F.	2-methyl tetrahydrofuran
n	normal
n.m.r.	nuclear magnetic resonance
Ph	Phenyl
ophen	ophenanthroline
P.P.N.	μ - nitrido - bis (triphenyl phosphine)
Pr	propyl
py	pyridine
R	alkyl or aryl group
t	tertiary
Td	tetrahedral
T.H.F.	tetrahydrofuran
T.H.P.	tetrahydropyran
t.m.s.	tetramethylsilane
U.V.	ultraviolet
w.r.t.	with respect to

NOMENCLATURE THE TERMS COBALTOUS, COBALTIC AND FERROUS USED THROUGHOUT THE THESIS REFER TO COBALT (II) COBALT(III) AND IRON(II) RESPECTIVELY.

CHAPTER 1

INTRODUCTION

CHAPTER 1 - INTRODUCTION

1. COBALT

Although not the most abundant element on earth (there is only 0.0023% in igneous rocks of the crust) cobalt has a long history. The word came into the English Language in 1728[1] from the German Kobalt, apparently derived from Kobald who was a goblin of the mines. This arose because the German miners of Saxony used the term to describe certain ores which injured their hands and feet and which was later found to contain arsenic cobalt ores[2].

An alternative explanation is given by H.C. Hoover, in his translation of "De Re Metallica" by Agricola, who states that cobalt is derived from the Greek word Cobalos meaning a mine.

Cobalt blue, as a colour description, has been known since 1835. The blue pigment has been found in early specimens of Egyptian and Babylonian blue glass[3], and pottery, as far back as 1450 B.C.[2]. It has been used in pottery and enamel trades both for colouring and for neutralising the yellow tinge in earthenware due to iron oxide. Cobalt salts have been used to colour ceramics, while combinations of cobalt, nickel, chromium or manganese give a range of blue to green colours.

The metal itself was isolated in 1735 by Brandt and in 1780 Bergman studied its properties. It is a hard blue/white metal, harder than steel, which resembles iron closely. When finely divided it is pyrophoric, although it is not attacked by water. In common with other group VIII elements it has a high melting point (1490°C) and a very high boiling point (3100°C), absorbs hydrogen, and has a marked catalytic power. It will also form complexes extremely readily. The only natural isotope is ^{59}Co, although ^{60}Co is used as a radioactive tracer in medicine, science etc. Cobalt is essential to life, the absence of the cobalt containing vitamin, vitamin B12, causing pernicious

anaemia. It also plays an important role in animal nutrition[4].

In minerals, cobalt is usually found with nickel, often as the arsenide.

It is one of three ferromagnetic elements (iron and nickel being the others) and although its permeability is about two-thirds that of iron, when it is alloyed with iron, nickel and other metals exceptional magnetic properties have been developed.

In the nineteenth century world output of cobalt was from Germany, Hungary and Norway. In 1864 Garnier discovered the oxidised ores of New Caledonia and these were developed in 1874. The next important source was discovered in 1903 in Ontario, Canada, and by 1904 this rich silver-cobalt ore was producing sixteen tons of cobalt. The Union Miniere du Haut Katonga in Belgium Congo initiated the extraction of cobalt from copper-cobalt ores in 1920 and this now is the leading cobalt producer along with Ontario[2,5].

Relatively little cobalt ore is mined for cobalt alone, i.e. most of the metal is recovered as a byproduct from ores treated for their copper, lead or nickel content.

Cobalt exists for a range of oxidation states, from -1 (in $[Co(CO)_4]^-$) to +4(in $[CoF_6]^{2-}$, also $[(NH_3)_5Co\text{-}O_2Co(NH_3)_5]\ X_5$ is thought to contain Co^{4+} although it could be regarded as a mixed valence species, e.g. $Co(III)O_2^{\cdot-}Co(III)$ or $Co^{3\frac{1}{2}}O_2^{-}Co^{3\frac{1}{2}}$).

Co^{2+}, the cobaltous ion, is the only d^7 ion of common occurrence. It is the most stable state of the simple ion when only water is the coordinating ligand. Compounds of the ion include cobalt oxide CoO ; cobalt hydroxide $Co(OH)_2$; cobalt sulphide CoS; cobalt fluoride CoF_2.

The numerous complexes of Co^{2+} fall into two types -

a) Pink, octahedral complexes e.g. $[Co(H_2O)_6]^{2+}$ and

b) Intense blue, tetrahedral complexes e.g. $[CoCl_4]^{2-}$.

Cobalt (II) forms more tetrahedral complexes than any other transition metal ion[6]. There are exceptions to these catagories, e.g. anhydrous $CoCl_2$ is blue but octahedrally coordinated; also other stereochemistries are possible e.g. square planar and five coordinate geometries. It is also possible to have two different geometries co-existing in one species e.g. complexes of pyridine.

For the cobaltous ion in an octahedral environment the ground state configuration can in principle be $t_{2g}^5 e_g^2$ (in weaker fields) - a high spin complex - or $t_{2g}^6 e_g$ (in stronger fields) - a low spin complex. The latter complexes are only expected if the ligands are very far to the strong end of the spectrochemical series, thus giving rise to the high values of ligand field strength required. A truly octahedral species under these conditions is unlikely because of the large Jahn-Teller distortion, i.e. Co^{2+} low spin complexes are rare, if not non-existent, certainly none have been structurally characterised. Low spin complexes have also a large antibonding effect of the e_g electron to overcome.

Tetrahedral cobaltous complexes are high spin regardless of ligand field strength[7].

Co^{3+}, the cobaltic ion, is a d^6 ion. Simple compounds of Co^{3+} are strong oxidising agents, and in water $[Co(H_2O)_6]^{3+}$ is very powerful, oxidising water to oxygen whilst being reduced to $[Co(H_2O)_6]^{2+}$;

i.e. $$[Co(H_2O)_6]^{3+} + e^- \longrightarrow [Co(H_2O)_6]^{2+} \; ; \; E^o = +1.84V \qquad (1.1)$$

Other ligands, e.g. ammonia, stabilise the +3 oxidation state to varying degrees in aqueous solutions, while ligands, such as CN^-, stabilise Co^{3+} to such an extent that cobalt (II) complexes will reduce water to hydrogen:

$$[Co(CN)_6]^{3-} + e^- \longrightarrow [Co(CN)_5]^{3-} + CN^- \; ; \; E^o = -0.8V. \qquad (1.2)$$

$[Co(CN)_5]^{3-}$ is a low spin paramagnetic complex.

Most of the known Co(III) complexes are octahedral, with few exceptions; there is a heteropolytungstate with Co(III) tetrahedral, which has an affinity for nitrogen donors. One of the most important cobaltic compounds is vitamin B12 which is coordinated to five nitrogens (four from the pyrroline rings and one from a benzimidozole ring) and the carbon atom of a CN^- group. This compound has a strong trans effect.

All Co(III) complexes known have diamagnetic ground states with the exception of $[CoF_6]^{3-}$ which is paramagnetic with four unpaired electrons.

Co(IV), a d^5 ion, is uncommon and to date does not have an extensive chemistry.

Co(I), a d^8 species, has only a few known complexes, all of which, except reduced vitamin B12 and cobaloximes, involve π - acid type ligands. The characteristic coordination number seems to be five with trigonal bipyramid being the preferred structure although octahedral and square pyramidal structures are also known.

This oxidation state can be achieved by disproportionation of dicobalt octacarbonyl using isonitriles, i.e.

$$Co_2(CO)_8 + 5RNC \longrightarrow [Co(CNR)_5]^+ [Co(CO)_4]^- + 4CO \qquad (1.3)$$

Various salts of the $[Co(CNR)_5]^+$ cation can be prepared by the action of excess of isonitrile on a cobaltous salt or by preparing $Co(CNR)_4X_2$ then reducing it with RNC, N_2H_4, $S_2O_4^{2-}$ or an active metal.

In solvents at elevated temperatures the cation $[Co(CO)_3(Ph_3P)_2]^+$ is formed from dicobalt octacarbonyl and triphenyl phosphine :

$$Co_2(CO)_8 + 2Ph_3P \longrightarrow [Co(CO)_3(Ph_3P)_2]^+ [Co(CO)_4]^- + CO \qquad (1.4)$$

This reaction also proceeds in non polar solvents, e.g. hexane, at 0^oC or below[8]:

$$Co_2(CO)_8 + PPh_3 \xrightarrow{\text{fast}} Ph_3P\overset{\delta+}{Co}(CO)_3 - \overset{\delta-}{Co}(CO)_4 \xrightarrow[PPh_3]{\text{v. fast}} [(Ph_3P)_2Co(CO)_3]^+ [Co(CO)_4]^- + CO \qquad (1.5)$$

The product on heating to 60°C under nitrogen will form the dimer $[Ph_3PCo(CO)_3]_2$, a red orange solid[9].

Cobalt in the zero oxidation state is found in carbonyls $[Co_2(CO)_8$ and $Co_4(CO)_{12}]$ and has been reported in the complex cyanide, $K_4Co(CN)_4$, which is easily oxidised in air[10].

Cobalt, and a variety of its complexes, are important industrially, especially in the role of catalysts. Dicobalt octacarbonyl is the catalyst precurser in the Oxo reaction i.e. hydroformylation of alkenes with hydrogen and carbon monoxide to yield aldehydes:

$$>C = C< + CO + H_2 \xrightarrow[100^{\circ}C, 100\ atm]{Co_2(CO)_8} -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{CHO}{C}}- \qquad (1.6)$$

Cobalt-molybdena-alumina (CMA) is used to remove sulphur from crude oils in catalytic hydrogenation units. Fluorination of hydrocarbons is achieved by passing them over higher metal fluorides e.g. CoF_3 (which is easiest to handle), MnF_3 or AgF_2. Cobalt catalysts are also commercially possible in polymerisation, oxidation, dehydration, hydrogen - sulphide production, nitrile synthesis, amination of alkenes and decomposition of acetylene.

80% of cobalt consumed is used in the manufacture of alloys and the remainder is used in pigments, salts, driers and ceramic frits.

2. METAL CARBONYLS

Organometallic chemistry, of which metal carbonyl chemistry is a precise branch, has been around for some time and undergone a number of definitions. One of the earliest was given by K. Krause and A. Von Grosse[11] in 1937:

'In the category of "metal-organic or organometallic compounds" is included a series of versatile, reactive materials in which a metal is bonded directly through at least one primary valence to the carbon atom of a hydrocarbon radical ..... Excluded by this definition are

the numerous metal containing organic compounds in which the organic part is bonded to the metal through oxygen or another non metal e.g. nitrogen, phosphorus or sulphur ..... Carbides, cyanides and metal carbonyls also do not belong to the class of organometallic compounds because they contain no hydrocarbon radical. A completely sharp line cannot be drawn between pure organic and metal-organic (such as Na_4C and $NaCH_3$) since there are also intermediate species e.g. Na_3CH and Na_2CH_2.'

The current definition of organometallic chemistry however includes metal carbonyls and their derivatives along with most metal carbon bonded species, the metal being main group or transition element.

The first organometallic compound was reported in 1760 by L.C. Cadet de Grassecourt[12], a Parisian military apothecary. This was cacodyl which he discovered when working on cobalt solutions for use as invisible inks. Its characterisation was carried out by Bunsen in the 1830's and later its name changed from alkarsin to cacodyl (Greek - foul smelling) and finally to tetramethyl diarsine[13] which is its present day systematic name.

The first recognised organometallic complex was Zeise's salt, $K[PtCl_3(C_2H_4)]$, prepared in 1827 by bubbling ethylene through tetrachloroplatinum.

In 1849 E. Frankland prepared diethyl zinc from ethyl iodide and zinc. Between 1850 and 1880 three main preparative routes were devised by Frankland which are still the basis of most organometallic synthesis[14]. These were:

$$2MeI + 2Zn \longrightarrow Me_2Zn + ZnI_2 \qquad (1.7)$$

$$2SbCl_3 + 3Me_2Zn \longrightarrow 2M_3Sb + 3ZnCl_2 \qquad (1.8)$$

$$Me_2Hg + Zn \longrightarrow Me_2Zn + Hg \qquad (1.9)$$

Frankland also used the rapid growth of knowledge during this period to formulate his concept of valence.

'When the formulae of inorganic compounds are considered, even a superficial observer is struck with the general symmetry of their construction; the compounds of nitrogen, phosphorus, antimony and arsenic especially exhibit the tendency of these elements to form compounds containing three or five equivalents of other elements, and it is in these properties that their affinities are best satisfied. .... Without offering any hypothesis regarding the cause of this symmetrical grouping of atoms, it is sufficiently evident .... that such a tendency valence law prevails and that, no matter what the character of the uniting atoms may be, the combining power of the attracting elements is always satisfied by the same number of these atoms'[15].

Twenty years later D. Mendeleyeev used alkyl metal compounds in the compilation of his periodic law, predicting the existence of elements which had not yet been discovered[16].

The first metal carbonyl complexes were cited in 1868, these being a series of platinum carbonyl chlorides[17].

By this time the Solvay process for production of sodium hydrogen-carbonate was commercially important. The byproduct was ammonium chloride and scientists were looking for ways of making chlorine from this. However the carbon dioxide stream used to sweep out ammonia was found to corrode the nickel valves of the reactor vessel. L. Mond and his co-workers[18] discovered that this was due to the action of carbon monoxide, present in the carbon dioxide as an impurity, on nickel forming a new type of complex - a pure metal carbonyl. This reaction took place at a temperature between 350 and 450°C to give a volatile nickel compound residue equivalent to nickel and carbon

monoxide, "which will be called nickel-carbon-oxide, of formula $Ni(CO)_4$". They showed that heating this compound in a mixture of gases decomposed it to nickel contaminated with carbon and that the $Ni(CO)_4$ vapour exploded violently at 60°C.

Experiments to make the carbon monoxide derivatives of other metals (e.g. Co, Fe, Cu and Pt) failed over the temperature range 15 to 750°C.

A year later, in 1891, iron pentacarbonyl was made from iron and carbon monoxide. It was independently discovered by Mond et al.[19] and Berthelot[20] whose papers were presented on 15th. June 1891 in London and Paris respectively.

The early part of the twentieth century saw a proliferation of metal carbonyl compounds. In 1905 and 1906 Dewer and Jones reported $Fe_2(CO)_9$ [21] and $Fe_3(CO)_{12}$ [22] from condensed $Fe(CO)_5$ and $Fe_2(CO)_9$ respectively; in 1910 Mond et al. made $Co_2(CO)_8$ (from cobalt and carbon monoxide) and $Co_4(CO)_{12}$ (from condensed $Co_2(CO)_8$ reported as having the molecular formula $Co(CO)_3$)[23]; in 1926 the formation of $Cr(CO)_6$ from a Grignard reaction on $CrCl_3$ [24], with the tungsten analogue reported two years later[25]. $Ru(CO)_5$ and $Ru_3(CO)_{12}$ were noted in 1936 [26] (although the original molecular formula assigned to this compound was $Ru_2(CO)_9$ with the correct version established by Corey and Dahl in 1963 [27]). Through the forties carbonyl complexes of iridium[28], rhenium[29], rhodium[30] and osmium[31] were reported. The compounds of manganese[32], vanadium[33] ($V(CO)_6$ being the first paramagnetic metal carbonyl, thus violating the Effective Atomic Number rule), tellurium[34] and mixed metal carbonyls e.g. $Co(CO)_4$-$Mn(CO)_5$ [35] and $Mn(CO)_5$-$Re(CO)_5$ [36] were discovered throughout the fifties and sixties. Excluding compounds of the formula $M_x(CO)_yL_2$ e.g. $Pt(CO)_2Cl_2$, the only transition elements described[37]

as known to form simple metal carbonyls at this time were titanium, copper, niobium, palladium, silver, tantalum, platinum and gold. From the beginning there has been controversy over the structures and nature of bonding in these compounds. Mond, Hirtz and Cawap[23] summarised the current knowledge of chemical properties in 1910 e.g. they all decomposed on heating to give the metal and carbon monoxide, they were not attacked by non oxidising acids, although quickly dissolved by oxidising acids with evolution of carbon monoxide and they were soluble in organic solvents (ether, ethanol and benzene), insoluble in water.

The authors also gave $Co(CO)_3$ as a molecular formula (for $Co_4(CO)_{12}$?) and suggested that $Mo(CO)_6$ was also only a molecular formula. In fact in a later paper it was mooted that the correct composition was $Mo_5(CO)_{26}$ or a similar large molecule[38]. Doubt was cast on theories that all carbonyl groups were directly bonded to the metal (for instance this would require cobalt to be eight coordinate) or that these compounds were ring structures:

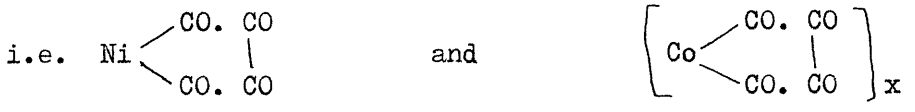


Figure 1.1

with molecular weight determinations against the latter idea.

During the next decade or so, various theories came and went. T.M. Lowry stated that when an atom contributed both electrons of a bond it would become positive with its neighbour becoming negatively charged (Ref: Chem & Ind., 42 (1923) 412). Langmuir proposed the ideas of sheaths of electrons i.e. outer shell electrons (Ref: Science, N.S.44 (1921) 64). This meant that transition metal atoms had sheaths of eighteen electrons and e.g. nickel in $Ni(CO)_4$ would have layers of electrons 2-8-8-18. This idea was extended by Welo and Baudisch

(Ref: Nature, 116 (1925) 606) who took the diamagnetism of $Ni(CO)_4$ to indicate an electronic structure of krypton, Kr(2-8-18-8). This provided a dilemma since the nickel kernel (Ni_{28}2-8-18) would be electronically neutral and so have no electrostatic attraction for the eight sheath electrons thus meaning that magnetic forces alone were holding together this outer layer.

In general, the maximum number of electrons in succeeding levels were 2, 8, 18 and 32 respectively with the outer layer collecting eight electrons but capable of supporting a greater number when there were positive charges of neighbouring atom kernels. The position of the electrons was fixed although the conception of electrons orbiting a central position had been put forward. This was thought unlikely since the centre of such orbits (i.e. the centre of electrostatic attraction) must lie at points between the two atomic nuclei. For some compounds this would require figures of eight or double loops. Another attempt to describe (vaguely!) the nature of bonding forces in molecules used the idea of secondary valency. This was applied when the primary valences were satisfied, particularly where an ordinary valence could not be assigned to each atom through a rearrangement of the bonds. $Ni(CO)_4$ was considered to be such a compound because its precise structure/valence was not defined. Valence was only precisely defined by kernel charge, number of electrons in the sheath and the number held in common with other atoms.

For the next twenty years various ideas regarding bonding and structure in metal carbonyls vied with each other, one of the most influential being the Effective Atomic Number (E.A.N.) rule, proposed by Sidgewick in 1927 [39] :-

'The first step is to determine how many electrons surround the

nucleus of an atom in a molecule of known structure, and how many of these are shared with other atoms. As the number in a neutral isolated atom is the atomic number, that in the combined atom (which will obviously vary with the state of combination) may be called the Effective Atomic Number (E.A.N.) ..... We have to find how the original atomic number of the atom in question is modified by the state of combination. We must therefore make the following changes in it:

(1) For every covalency, due to the attachment of a univalent radical, we add one.

(2) For every coordinate valency, such as is formed by attaching the atom to a complete molecule, when the atom acts as accepter we add two: when it acts as donor, no change is made.

(3) If the resulting complex is an ion, we add the value of its negative or subtract that of its positive electrovalency.

This was being challenged by 1938, with objections being raised about the high negative charge on the central atom (e.g. $[Co(NH_3)_6]^{3+}$ has as the central atom Co^{3-}) and the donor properties of lone pairs on water and ammonia (according to the above theorem these are stable closed shell structure)[40]. Nowadays this rule has been modified with reference to transition metal complexes. The central atom in a complex has the same number of electrons available as the next noble gas, this total being made up from its own electrons, electrons obtained by donation (from lone pairs or pairs of electrons from π bonding systems), by covalent bonding (each covalent bond contributing a single electron) and taking into account the overall charge on the complex; e.g. in $Fe(CO)_5$ iron has its core electrons plus eight valence electrons in addition to the ten electrons donated by the five carbonyl groups to reach the E.A.N. For the transition element series, this rule is also known as the eighteen electron rule (w.r.t. the eighteen valence electrons of Kr, the nearest noble gas). With new synthetic techniques,

this rule is often violated with sixteen, seventeen and even fourteen electron complexes being formed.

Langmuir had already suggested[41] that there might be double bonding between nickel and carbon in $Ni(CO)_4$ and evidence for the resultant shorter than normal single M — C bond was established through electron diffraction studies of metal carbonyls by Brockway and co-workers[42,43]. This led to the idea of resonance structures i.e.

$Ni\text{-}C \equiv O \longleftrightarrow Ni = C = O$ which was fully developed in the 1950's.

In the 1940's there was great discussion about the nature of bonding in metal carbonyls[44]. Exchange reactions with bulk carbon monoxide indicated that the carbonyl groups retained their identity in the organometallic entity and although there was doubt about the formal valency of the metal, there was a definite relationship between the composition of the simple metal carbonyls and the position of the metal in the periodic table. The zero dipole moment in $Ni(CO)_4$ was taken to mean collinearity of the Ni — C — O bonds which existed as $\bar{N}i - C \equiv \overset{+}{O}$ moiety. The possibility of $Ni = C = O$ was considered but dismissed because it would mean high covalencies for polynuclear iron and chromium compounds. Bond lengths and Raman spectroscopy favoured the initial structure containing $C \equiv O$ but the shorter than expected M — C bond favoured resonance between the two possible electron distributions. Only in $Ni(CO)_4$ could all the carbonyl groups coordinate to the metal centre in a $M = C = O$ arrangement (favoured because of avoidance of an accumulated negative charge on the metal); the ketene like structure would decrease in importance for $Fe(CO)_5$ and $M(CO)_6$ compounds. $M(CO)_6$ was known to form regular octahedral structures[45] but there were doubts about $Fe(CO)_5$ being trigonal bipyramidal[43], as hinted by electron diffraction work, because it was thought to have a small dipole moment.

There was also the possibility of Pauling's hypotheses - that there were four or six equivalent σ type bonds in coordination compounds which come about by hybridisation of d, s and p type orbitals, thus making the spatial arrangement of coordinated groups an index of bond type. Polynuclear metal carbonyls and nitriles were also under scrutiny.

To meet the requirements of the E.A.N. rules it was suggested that all metal centres had to acquire an E.A.N. of an inert gas and the carbonyl group could form two collinear coordinate links. Polynuclear compounds were formed because of the inability of the metal to obtain a closed electronic configuration (i.e. it had an odd atomic number) or the compound had a smaller carbonyl : metal ratio than the maximum possible. However this latter generalisation was being violated even in 1948 by known compounds e.g. $Fe_2(CO)_9$.

By the above rules $Fe_2(CO)_9$ would exist as two $Fe(CO)_4$ units linked by a bridging carbonyl group, i.e.

$$(OC)_4Fe \longleftarrow C \equiv O \longrightarrow Fe(CO)_4$$

The ligand CN^- was known to form such links but carbon monoxide in the same role involved residual positive charges on adjacent carbon and oxygen atoms therefore making this less likely. In 1929, Brill[46] had suggested that $Fe_2(CO)_9$ had trigonal symmetry and this had been verified by X-Ray studies[47]. From this the bridging carbonyl structure, shown in Fig. 1.2, was established violating the Sidgewick rules.

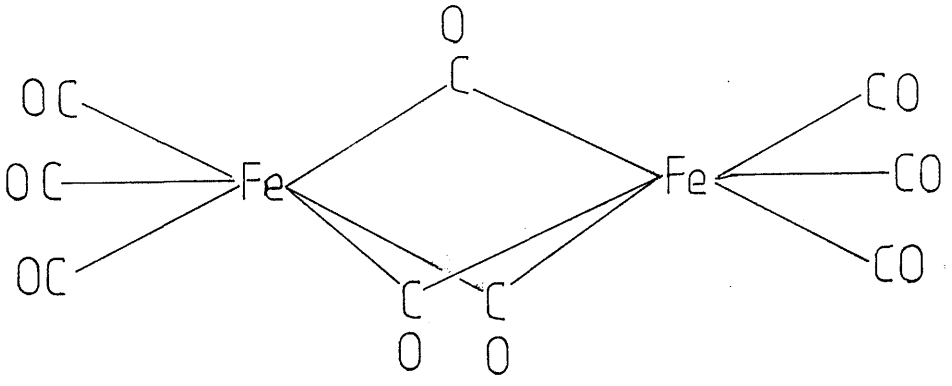


Figure 1.2

Here the bridging carbonyl groups have double bond character while the terminal carbonyls retain their triple bond, the evidence coming from bond length studies. Thus each iron atom forms three covalences to give an E.A.N. of 35 leaving one unpaired electron. As the compound is diamagnetic, spin coupling between the two relatively close iron atoms was postulated.

Although these suppositions were plausible for $Fe_2(CO)_9$ problems arose when they were applied to $Co_2(CO)_8$ (because of unpaired electrons), $Co_4(CO)_{12}$ and $Fe_3(CO)_{12}$ etc. $Fe_3(CO)_{12}$ was considered to have two - fold symmetry resulting in the structure of Fig. 1.3

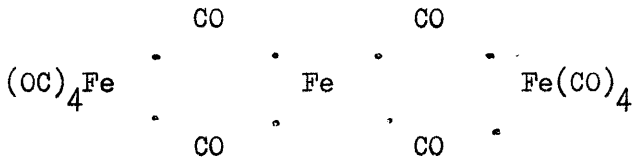


Figure 1.3

The central atom would be quadrivalent with an E.A.N. of thirty giving a paramagnetic compound. Distinction between two substantially different kinds of metal - CO binding within polynuclear carbonyls was considered to be out of step with the general chemistry of such compounds, when compared with the simple carbonyls.

The possibility of resonance was again raised, by Jensen[48], i.e.

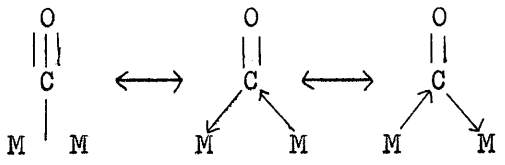


Figure 1.4

Now $Fe_2(CO)_9$ could be represented as a resonance hybrid.

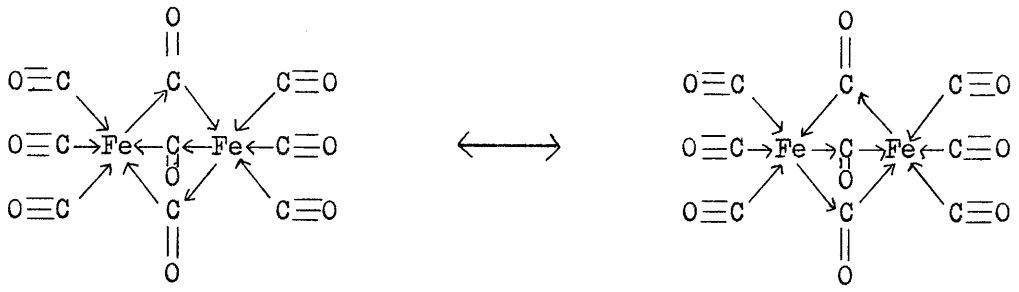


Figure 1.5

Finally work in 1948 verified Brill's original suggestion with three bridging carbonyls and an iron - iron bond[49].

Bridging carbonyls were also mooted for $Co_2(CO)_8$ (see later), $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ [29]. Investigation of the infrared (i.r.) spectra of the latter two compounds by Dahl and his co-workers[50] showed there to be no absorptions in the bridging carbonyl region (around 1850 cm^{-1}). From this and other structural information they deduced that these compounds had one metal - metal bond and five metal - carbonyl bonds, the carbonyls being in a staggered conformation around the central atoms. The known diamagnetism of the compounds, the agreement between the observed i.r. spectra and the calculated i.r. absorptions, and the conformity of the compounds with the E.A.N. rule all lent support to the proposed structure.

In the early sixties vanadium hexacarbonyl, one of the last unknown simple metal carbonyls, was synthesised and its structure determined. Although first prepared in 1959 and 1960 by various groups its composition remained a mystery. One idea put forward was that it was dimeric i.e. $V_2(CO)_{12}$ on the basis of molecular weight investigation, nuclear magnetic resonance (n.m.r.) and electron paramagnetic resonance (e.p.r.), the latter suggesting that the compound was diamagnetic[51]. This was later found to be a solvent effect and that the correct structure in the crystalline form was the monomeric form $V(CO)_6$, which was paramagnetic, as borne out by X Ray diffraction and magnetic

susceptibility studies[52].

By now a great deal of work was being done to help understand the structure and bonding of such compounds and to use this information to synthesise the unknown metal carbonyls of the day. One side issue of this increase in knowledge was the loss of carbon monoxide's uniqueness as a ligand for transition metals when other ligands, e.g. hydrocarbons, phosphines and arsines were found, to varying degrees, to stabilise the lowest oxidation states of these elements.

The use of $d\pi - p\pi$ bonding to explain structures was now coming to the fore. As only transition metals possessed available d orbitals (in contrast to main group metals) this restricted formation of such bonded structures to transition metals. The stability of the metal carbonyl bond was due to the back donation of electrons from the metal d shell to the ligand giving rise to $M = C = O$ or $\overset{+}{M} \equiv C - O^{-}$ resonance forms of $^{-}M - C \equiv O^{+}$. Whereas back donation in carbonyls involves overlap in the nodal plane (leading to a true π bond), unsaturated hydrocarbons involved the π orbitals at right angles to the nodal plane which is more accurately described as a μbond which is largely dative in character. This would mean increased stability of mixed carbonyl/unsaturated hydrocarbon transition metal complexes because of the mutual interaction of the two types of ligands[53].

Pure metal carbonyls were now being assigned to one of nine groups depending on structure. These were:

(i) $M(CO)_4$ (ii) $M(CO)_5$ (iii) $M(CO)_6$ (iv) $M_2(CO)_8$ (v) $M_2(CO)_9$
(vi) $M_2(CO)_{10}$ (vii) $M_3(CO)_{12}$ (viii) $M_4(CO)_{12}$ (ix) $M_6(CO)_{16}$.

The types of linkages involved in such structures were classified as

(1) Covalent metal - metal bonds with each metal supplying one electron.

(2) Coordinate covalent σ type metal - carbon monoxide bonds with the carbon atom donating one pair of electrons to the metal and receiving

partial π type back bonding from the d electrons of the metal.

(3) Covalent σ type metal - carbon monoxide bonds with the carbon atom as a bridge between two metal atoms and forming a bond with each.

A fourth possibility in $M_6(CO)_{16}$ complexes was a triply bridging carbon monoxide group (i.e. bonding to three metals). Such compounds also were a large deviation from the E.A.N. rules[37].

Podell has shown[54] that the thermal stability of metal carbonyls decreases in going from left to right across the periodic table according to:-

Even Z	$Cr(CO)_6 > Fe(CO)_5 > Ni(CO)_4$
Odd Z	$Mn_2(CO)_{10} > Co_2(CO)_8$

and that the ease of formation of a metal - carbonyl bond is based upon the rate of reaction of the metal with carbon monoxide giving rise to the sequence:-

Even Z across	Cr < Fe < Ni
Even Z down	Cr < Mo < W
Odd Z across	V < Mn < Co

Nyholm had drawn up his set of "rules" for metal - ligand bond stability[55].

a) metal must have available electrons in suitable d orbitals, therefore for non bonding configuration d^n, the number of <u>possible</u> double bonds decreases as n approaches zero (thereby explaining the non existence of non transition metal carbonyls).

b) the ligand must have empty d (as in R_3P) or p orbitals which can be made available (as in carbon monoxide) to receive these d electrons.

c) the sizes of the orbitals must be such as to ensure effective overlap.

The ability of metals to form π-d bonds varies with $Ni^o \gg Pt^o \geqslant Pd^o$, $Au^+ > Cu^+ > Ag^+$ and zero valent metals > covalent metals > tervalent metals.

Gradually a more sophisticated picture of bonding developed. Bonding in metal carbonyls involved three possible bonds - the C-O bond, the

M-C bond and the M-M bond[56].

a) C-O Bond

Carbon monoxide has three occupied σ orbitals[57] (i) σ bond between the two atoms; (ii) the lone pair of electrons on the carbon and oxygen atoms; (iii) the doubly degenerate bonding π orbital. These overall add up to a triple bond $(\sigma)^2(\pi_y)^2(\pi_x)^2$ as shown in Fig. 1.6.

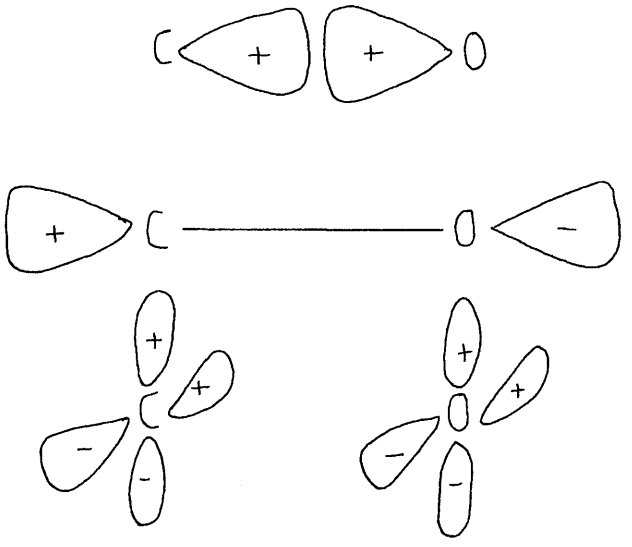


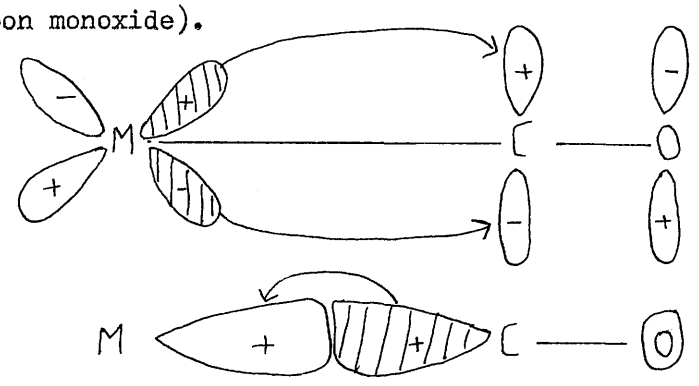
Figure 1.6

This is an over simplification since the lone pair on oxygen is probably not as strongly directed as the corresponding lone pair on carbon, which is almost entirely a diagonal C(2s) - $C(2p_x)$ hybrid. There is unequal electronic charge distribution in the π orbitals, the electrons being four times as likely to be nearer the oxygen. This leads to a fairly polar bond with considerably lower strength than in a smiilar homonuclear triple bond e.g. N_2.
Carbon monoxide has however a low dipole moment because the bond polarity compensates for the strongly directional lone pair of carbon.

b) M-C Bond

Carbon monoxide does not appear to be basic in nature and the donor power of the lone pair of electrons in carbon is slight, leading to

a general absence of simple complexes with the normal vacant orbital accepters. Because of this low basicity, the overlap of the lone pair on carbon with nd, (n+1)s and (n+1)p vacant metal orbitals is not enough to constitute as stable a metal - carbon σ bond as found in metal carbonyls. So an additional π bond, formed by back donation of charge from the filled non bonding d orbitals of the metal to the empty π anti bonding orbitals of carbon monoxide, is postulated. This will increase the bond strength in two ways - firstly by the addition of a bond and secondly by removing the unfavourable charge separation induced by the donor σ bond thus strengthening the σ bond which in turn leads to more extensive back bonding. This type of interaction between two types of bonding reinforcing each other is synergic bonding. (in main group chemistry borane carbonyl, H_3BCO, is known, its stability being attributed to hyperconjugation of the BH_3 group and π bonding with the carbon monoxide).



π bond formation

σ bond formation

Figure 1.7

This type of bonding has two requirements; that symmetry must be such that the σ and π parts of the bond match and energy considerations will allow a good overlap. The effect on the bond order is to decrease the strength of the C-O triple bond and so the i.r. carbonyl frequencies of metal carbonyls is lower than that of the isolated carbon monoxide ($\bar{\nu}$(CO) 2155 cm^{-1}, $\bar{\nu}$ (MCO) 2000 cm^{-1} for terminal CO, $\bar{\nu}$ (MCO) $\sim$1850 cm^{-1} for bridging CO of even lower bond order).

To induce an effect in either of the M-C or C≡O bonds will naturally affect the other bond in the opposite sense. This is seen in the isoelectronic series $Ni(CO)_4$, $[Co(CO)_4]^-$ and $[Fe(CO)_4]^{2-}$ where there is a steadily increasing excess of negative charge. This increases the extent of M-C back bonding and so increases the M-C bond order, simultaneously decreasing the C-O bond order. The effect is reflected in the i.r. absorption frequencies and force constants. As has already been seen, carbonyl groups can indulge in bridging, especially symmetrically, between two or more metal atoms, this effect being most pronounced with first row transition metals. In this instance the σ bond contains one metal electron plus one carbonyl electron, and the π bond becomes more complicated. Overall there is a decrease in C-O bond order, as observed by infrared spectroscopy.

c) M-M Bond

Frequently this is the only bond between two halves of the molecule, as in $Mn_2(CO)_{10}$ but it is also found in conjunction with bridging carbonyl groups as exemplified by $Co_2(CO)_8$. In the latter the M-M bond explains the diamagnetism of the binuclear species and allows the E.A.N. rules to be observed (diamagnetism alone only requires weak coupling of unpaired spins for which the bridging carbonyl groups could account).

Pure metal carbonyls are different from compounds with other ligands in that they obey the E.A.N. rule. Although this is a useful concept it is not inviolate as shown by the paramagnetic $V(CO)_6$. Metals have also been known to form carbonyl complexes with fourteen or sixteen electrons in the "closed shell".

Structure determinations, mainly by electron and X Ray diffraction techniques, suggest the linearity of the M-C-O group when the carbonyl groups are terminal or the bridging carbonyl groups are symmetrical.

Infrared spectroscopy has not only shown the effect of bridging carbonyl groups on absorption frequencies, but also shown a lower bond order for the C-O bond when strongly electron donating ligands, e.g. phosphines and amines,are present in the complex. These ligands presumably favour stronger back donation of electrons from the metal to carbon monoxide, therefore lowering the C-O bond order to a value approximating to that of normal "ketonic" carbonyls[58].

Metal carbonyls can, and do, undergo a variety of reactions, many of which are very important in organic synthesis and catalytic reactions. They are strongly covalent in character as shown by their volatility, their solubility in many non polar solvents and their insolubility in polar solvents. In many reactions they behave as distinct metal and carbon monoxide groups, forming an extensive range of addition, substitution and rearrangement complexes, under alkaline or acidic reaction conditions.

Carbon monoxide forms stable complexes with only the lowest oxidation states of the metal and so the metal is frequently in the zero oxidation state. The metal carbonyl moiety is susceptible to attack at any, or all, of its three centres with four possible sites of attack:

a) The metal - carbonyl bond -cleavage of this leads to M + CO fission.

b) Electrophilic carbon - attack by nucleophiles.

c) Oxygen lone pairs - these are potential nucleophiles and Lewis bases.

d) The metal - a potential Lewis base, especially in its low oxidation state.

As thissystem is conjugated, reaction at any one site will affect the others.

Much of the early work in this field of chemistry was carried out by the late Walter Hieber and his team, from the late 1920's through to the sixties and seventies. A small sample of the varied work includes

substitution reactions with isonitriles, trihalides and triaryls of the phosphorus[59], reactions with bases[60], the formation of the hydrides of $[Co(CO)_4]^-$ and $[Fe(CO)_4]^{2-}$ [61], and the preparation and reactions of $Fe(CO)_5$ [62]. Methods of synthesis of various compounds and their history were reviewed by him in 1942 [63] and he showed that the strength of the base affected the product of reaction[60].

Strong Base: $3Co(CO)_4\,[\text{dimer}] + 2OH^- \longrightarrow 2CoH(CO)_4 + Co(CO)_3[\text{tetramer}] + CO_3^{2-}$ (1.10)

Weak Base: (e.g. NH_3) $3Co(CO)_4 + 2H_2O \longrightarrow 2CoHCo(CO)_4 + Co(OH)_2 + 4CO$ (1.11)

Similar investigations were mounted in the 1950's by H.W. Sternberg et al. [64].

"CO" insertion reactions, more accurately described as alkyl migration reactions, also aroused interest. Isotopic labelling was used in $RMn(CO)_5$ to establish that the entering carbon monoxide molecule is not the same carbon monoxide involved in the insertion between the metal and the alkyl group, but rather alkyl migration occurs[65]. The acyl species formed is an important intermediate in hydroformylation reactions.

A possible route is shown below[66], the detailed structure of the intermediates is unclear.

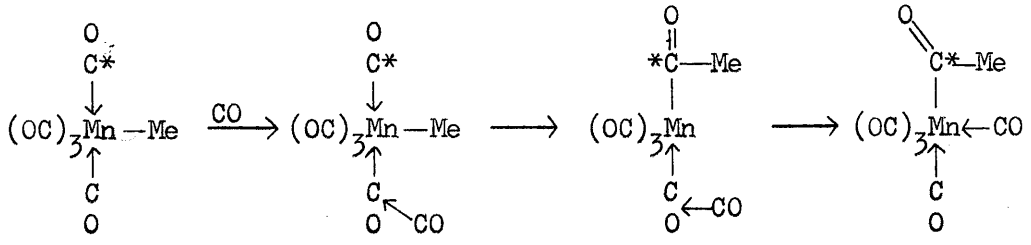


Figure 1.8

Not only alkyl metal carbonyls but also acyl and aryl metal carbonyls can undergo this type of reaction.

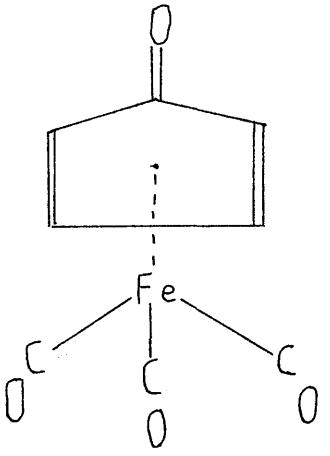
Carbon monoxide can be displaced by hydrocarbon ligands especially cyclopentadiene (cp) which was the only ligand then known to totally displace carbon monoxide from metal carbonyls (M = Cr, Fe, Co, Ni) to yield cp_2M[58].

Disproportionation reactions are also important. The general pattern of this type of reaction is typified by the equation:

$$2M(CO)_n + 6L \longrightarrow [ML_6]^{2+} [M(CO)_{n-1}]^{2-} + (n+1)CO \qquad (1.12)$$

This is the commonest mode of reaction of cobalt and iron, but chromium, manganese or nickel compounds require aqueous caustic alkalis. L is commonly a mild base with amines, piperidines and alcohols also able to initiate the reaction to some extent.

Reactions with acetylenes are important catalytically. Reppe discovered that $Fe(CO)_5$ plus acetylene in aqueous alcohol, and under pressure, gave a compound that hydrolysed at 80°C to give hydroquinone and the compound below[67].



This type of reaction can be controlled to produce organic compounds of the desired stoichiometry, e.g. the Reppe carbonylation process:

$$C_2H_2 + CO + ROH \xrightarrow{Ni(CO)_4} CH_2 = CH - COOR \text{ , } R = H, Alkyl, Aryl. \qquad (1.13)$$

By 1961 there were four main preparative methods for metal carbonyls[68]. These were:

1. Direct addition reaction $M + CO \longrightarrow M-CO$ e.g. where M = Ni.

2. Displacement or abstraction reaction,

   a) $MX + 2CO \longrightarrow M-CO + X-CO$ e.g. where M = Ir, Re.

   b) M - ketyl + $CO \longrightarrow M-CO$ + ketone e.g. M = Mn.

3. Reductive carbonylation reaction, $MX + R + CO \longrightarrow M-CO + RX$ where R is an organometallic reagent (PhMgBr or Et_3Al) which will form a stable intermediate of M or a metal reducing agent which will stabilise a lower oxidation state of M w.r.t. carbonylation (e.g. Al - $AlCl_3$ couple) or an inorganic reducing agent e.g. $Na_2S_2O_4$.

4. Exchange reaction, $MX + Fe(CO)_5 \longrightarrow M-CO + FeX$.

Polynuclear metal carbonyls in general are formed by loss of carbon monoxide from the simpler metal carbonyls.

An array of techniques have been used to establish the composition of a complex as well as its structure, physical and chemical properties. For carbonyl compounds one of the most important, as already hinted, is infrared spectroscopy and, to a lesser extent, its near relative Raman spectroscopy. Their advantage is due to the manner in which the slightest change of the environment of the carbonyl group, be it the metal, different ligands within the compound or solvent effects, will show up sharply in the spectrum. N.m.r. spectroscopy becomes important when certain elements are present in the compound, usually ^{1}H or ^{19}F and to a lesser extent ^{31}P. With the improvement of technology, machinery to probe the more elusive isotopes suitable for n.m.r. will become more accessible. To date ^{17}O, ^{59}Co and ^{195}Pt n.m.r. studies are becoming more frequent.

In the earlier work of establishing exact compositions of molecules magnetic susceptibility studies also played a role. Radio isotope studies contributed to the effort, especially in exchange studies such as were used to replace the myth of "CO insertion" by the alkyl

migration mechanism. Similar data were used to verify existance of carbonyl groups in significantly different environments within the same molecule. An example of this was the system $Mn(CO)_5X + CO$ which showed the manganese to have four reactive carbonyl groups and one less reactive group. This was due to the trans effect of the halide, making the opposite M - C bond stronger and therefore harder to break[69]. Thermochemical and thermodynamical derived information were used to establish bond strengths e.g. the heat of combustion of $Fe(CO)_5$ was used to confirm that bonding in metal carbonyls resembled M::C::O [70]. Other techniques including X Ray diffraction, electron diffraction, and microanalysis have of course been used to great effect.

Metal carbonyls have been used industrially for many years. The Fisher - Tropsch process, to convert water gas to hydrocarbons[71] has been known since 1925 (equation 1.14):

$$CO + H_2 \longrightarrow \text{low weight alkanes, alkenes and alcohols} \qquad (1.14)$$

The Oxo process is used industrially for the conversion of olefins, with synthetic gas and a cobalt carbonyl catalyst, into homologous aldehydes or alcohols. This was stimulated by work by Reppe[67,72] who showed that $Ni(CO)_4$ could be used to generate carbonyl containing compounds from acetylenes.

Ferrocene, discovered in 1951 by two independent groups[73,74], heightened interest in transition organometallic chemistry. Both groups proposed its structure to be Fig. 1.9 (a) but it was Wilkinson et al. who deduced the accepted structure the following year (Fig. 1.9 (b)).[75]

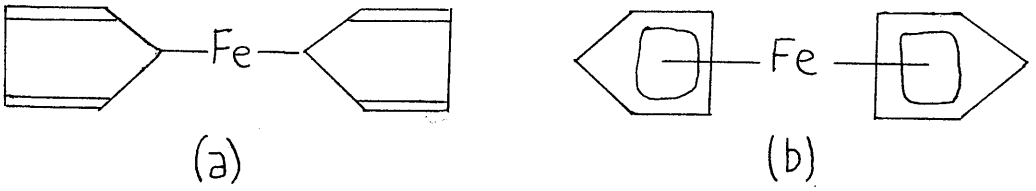


Figure 1.9

With this new type of bonding brought to their attention, chemists paid closer attention to transition metal chemistry. This resulted in a proliferation of new organic synthesis which utilised organometallic compounds of all kinds under a host of reaction conditions to give the desired product. Direct carbonylation reactions became important and are summarised in ref. 76 .

There are numerous organic reactions involving organometallic compounds. The beauty of using transition metal complexes in organic synthetic reactions is that it is often only a simple "one pot" reaction that is required to join two or more organic molecules in the desired manner instead of the conventional organic chemistry method which involves many stages. The former method will lead to quicker, cleaner and higher yielding reactions because of the simplicity of technique.

Metal carbonyl reactions have been used to disprove popular theories. Originally it was thought that no σ bonded organometallic compounds existed, mainly because the M - C σ bond was regarded as being too weak. The theory was then refined to include such compounds, when stabilised by π acceptor ligands[77]. Finally, the study of photochemical decomposition of transition metal compounds, including $Mo(CO)_6$ and the formation of such compounds involving only M - C σ bonds were used to disprove the doctrine of inherent instability. The first species reported as containing only M - C σ bonds were CrR_4 and MoR_4, R = $-CH_2SiMe_3$ [78a] although the crystal structure of the latter later proved it to have the composition Mo_2R_6 [78b]. The direction of research was then shifted towards reasoning why such compounds were unstable, what conditions and/or ligands would stabilise them, and not towards why the M - C bond was so weak[79].

There are still many facets of organometallic chemistry to be investigated, and old ideas revised in the light of new information, in what is one of the fastest growing branches of chemistry.

3. COBALT CARBONYLS

Cobalt carbonyl compounds have been present in the literature, under many guises, since the beginning of the twentieth century. The simplest mixture of carbon monoxide and cobalt is dicobalt octacarbonyl, $Co_2(CO)_8$, which first appeared in scientific journals in 1910 [23], having been made from its pure components. Another simple cobalt carbonyl, tetracobalt dodecacarbonyl, $Co_4(CO)_{12}$ was reported in the same paper. In present times there is a wide range of such compounds. Apart from the neutral compounds mentioned above there are anionic species e.g. $[Co_6(CO)_{15}]^{2-}$, cationic species, e.g. $[Co(CO)_3(PPh_3)_2]$, hydrides, $HCo(CO)_4$, carbido cobalt carbonyls e.g. $Co_6(CO)_{12}CS_2$, mixed metal carbonyls, e.g. $CoMn(CO)_9$ which was the first neutral mixed metal carbonyl containing only two transition metals plus carbon monoxide, and so on. Biologically vitamin B12 is an enlightening example of important organocobalts. When studied by X Ray crystallography in 1961 [80] it proved to be the first compound with a M - C bond found in a natural material.

Most of the early work on cobalt carbonyls, as on many metal carbonyl systems, was conducted by W. Hieber and his team, resulting in Hieber being regarded as the initiator of this field. By his own admission he was working with a class of compounds which were not categorised as such, and for many people were just curiosities[81].

Early work embraced the action of amines and ammonia on $Co_2(CO)_8$ over a period of years[82a], leading to the recognition of the disproportionation reaction and its potential usefulness in preparative metal carbonyl chemistry.

$$3Co_2(CO)_8 + 12NH_3 \longrightarrow 2\,[Co(NH_3)_6]\,[Co(CO)_4]_2 + 8CO \qquad (1.15)$$

$$\text{i.e. } 3Co^0 \longrightarrow Co^{2+} + 2Co^-$$

Better synthetic ways to $Co_2(CO)_8$ were now being sought. The standard method of passing carbon monoxide over finely divided (and carefully reduced) cobalt metal was not the easiest way because of problems of reducing the metal, and of special equipment needed to handle the relatively high temperatures and pressures ($\sim$ 200 atm at 200°C) which would not react with the starting materials. Hieber developed the method of using cobalt sulphide with carbon monoxide at 200°C and 200 atm pressure, eliminating one of the problems (re the metal purification).

$$2CoS + 8CO + 4Cu \longrightarrow [Co(CO)_4]_2 + 2Cu_2S \qquad (1.16)$$

with the copper itself being provided by the autoclave lining[82b]. The drawback was that any water present led to the formation of the hydride $HCo(CO)_4$. An alternative preparation was the action of carbon monoxide on CoX_2(X = I, Br, Cl) in the presence of other metals to facilitate ease of elimination of the halogen.[81] e.g.

$$CoBr_2 + 2Ag \longrightarrow Co + 2AgBr \xrightarrow{CO} [Co(CO)_4]_2 \qquad (1.17)$$

By now interest in this field had been aroused with a number of different groups contributing. H.W. Sternberg et al. became involved with reactions of $Co_2(CO)_8$ with bases. Disproportionation would occur when $Co_2(CO)_8$ was treated with pyridine.

$$12C_5H_5N + 3[Co(CO)_4]_2 \longrightarrow 2[Co(C_5H_5N)_6]^{2+} + 2[Co(CO)_4]^- + 8CO \qquad (1.18)$$

Further reaction with excess dilute sulphuric acid gave the unstable $HCo(CO)_4$ [64], which decomposes rapidly above its melting point (-26°C) to $Co_2(CO)_8 + H_2$.

The same group later reported the effect of using dimethyl amine as the base[83]. They had already established that Lewis bases initiated disproportionation under mild conditions, i.e.

$$12B + 3[Co(CO)_4]_2 \longrightarrow 2[Co(B)_6][Co(CO)_4]_2 + 8\,CO \qquad (1.19)$$

where B = H_2O, MeOH, EtOH, NH_3, pyridine or $\frac{1}{2}$o-phenanthroline.

However when B was dimethyl amine the carbon monoxide liberated appeared as dimethylformamide (at $0^{o}C$ and 1 atm pressure). The conclusion was that the reaction proceeded via a complex intermediate involving the carbonyl group of the metal carbonyl and the NH of the base.

The amount of carbon monoxide liberated during the disproportionation coincided with the amount required for reaction with dimethyl amine. This meant that the overall stoichiometric equation became:

$$3\left[Co(CO)_4\right]_2 + 24Me_2NH \longrightarrow 2\left[Co(Me_2NH)_6\right]\left[Co(CO)_4\right]_2 + 8HCONMe_2 + 4Me_2NH \text{ complexed} \qquad (1.20)$$

Naively it was presumed that only 20 moles of the base were required but experimental evidence pointed to the stoichiometry of equation 1.20. The extra four moles of base were necessary for complex formation between the carbonyl groups of the cobalt carbonyl anion and dimethyl amine, as shown by i.r. spectra. In excess amine all carbonyl groups appear to be complexed with the amine and carbon monoxide is released in the form of the amide. An intermediate salt is formed according to equation 1.21.

$$\left[Co(CO)_4\right]_2 + \text{excess } Me_2NH \longrightarrow \left[Me_2NHCo(CO)_4\right]^+\left[Co(CO)_4\right]^- \qquad (1.21)$$

The carbon monoxide moiety is transferred to the amine via this intermediate cation and so is not observed as a free entity.

Small amounts of $Co_2(CO)_8$ act as a catalyst in the production of urea from dimethyl amine, possibly via dehydrogenation:

$$2Me_2NH + CO \xrightarrow{Co_2(CO)_8} Me_2NCONMe_2 + H_2 \qquad (1.22)$$

An alternative mechanism involved the formation of a cobalt - dimethyl amine intermediate which would undergo "CO insertion" to give $CoCONMe_2$ which in turn would decompose to the urea[84].

A great deal of effort was being devoted to establishing the structure of $Co_2(CO)_8$. Initially the idea of a ring system was put forward, but was not received favourably because of conflicting evidence of molecular weight determinations[23]. In 1948, after discussing the structure of

$Fe_2(CO)_9$ and concluding that two $Fe(CO)_3$ groups were linked by three carbonyl bridges and an Fe - Fe bond, the author of the paper stated[49] 'it would be curious if this rare type of M - M linkage was confined to $Fe_2(CO)_9$, but it appears to exist in other compounds e.g. dimeric and diamagnetic cobalt tetracarbonyl $[Co(CO)_4]_2$ is formulated as illustrated. With cobalt, one electron more than iron, one less carbonyl bridge is required to obtain an isoelectronic structure (E.A.N. = 36) with the metal atom being similar to diamagnetic $K_3[Co(CN)_6]$ and diamagnetic iron compounds above.'

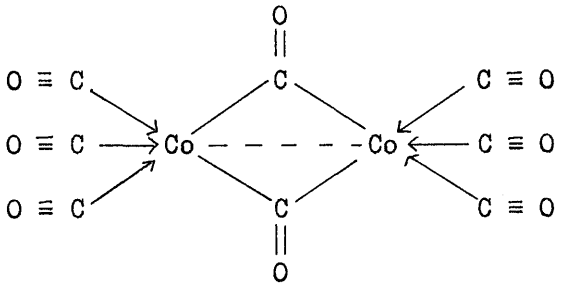
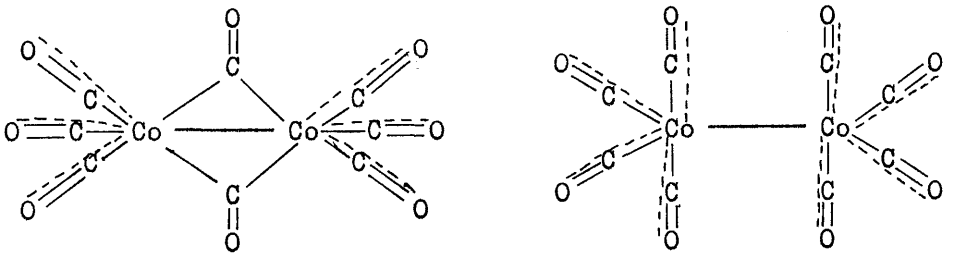


Figure 1.10

The idea of bridged and non bridged structures came into being and postulates were tested by i.r. and group theory calculations to substantiate whatever view was being forwarded. The two structures suggested were:



(a) (b)

Figure 1.11

the former being akin to the proposed shape of $Fe_2(CO)_9$[49] and comprised of two trigonal bipyramids joined at an edge. An i.r. study of the gas and solution phases of $Co_2(CO)_8$ was undertaken to clarify the issue[85]. This showed three bands at 2053 cm^{-1} and a single band at 1876 cm^{-1} in the gaseous phase, with lower frequencies observed for the solution spectrum; these were assigned to the terminal carbonyls and bridging carbonyls respectively. With quantitative analysis of the ratio of the two types of carbonyls (of 2:6 for bridging : terminal) and extensive results collected over a range of concentrations in both gaseous and solution phases, the authors favoured a bridging carbonyl structure although not totally discounting a non bridged structure.

The structure of $Co_2(CO)_9$ HC:CH was published in 1959[86] which led to a rethink about the structure of $Co_2(CO)_8$. The crystal structure showed each cobalt to be surrounded by five carbon atoms in a square pyramidal configuration. When two units are joined together the carbonyls are eclipsed and the two metal atoms are bridged by a carbon atom of a ring, i.e.

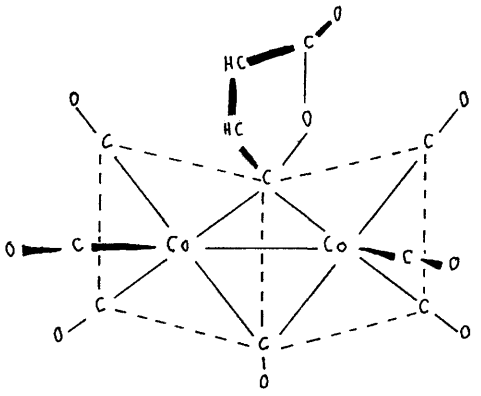
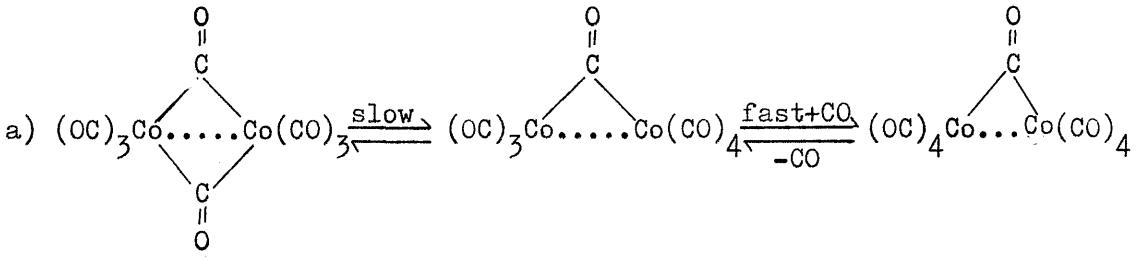


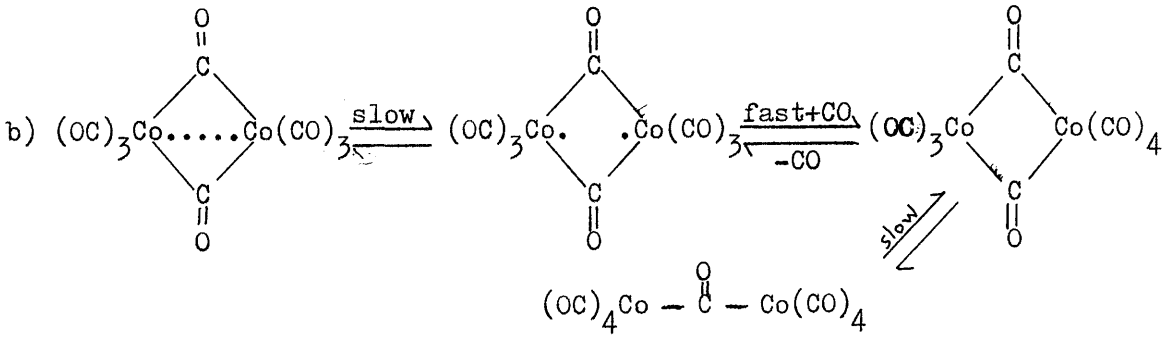
Figure 1.12

It was because the metal atoms and the bridging carbon atoms were not coplanar that doubts were cast about the structure of $Co_2(CO)_8$.

Basolo and Wojcicki then investigated the liability of the carbonyl ligands using $^{14}C \equiv O$ exchange[87] for both $Co_2(CO)_8$ and $Ni(CO)_4$. For the nickel case they found that the rate of exchange did not depend upon the concentration of carbon monoxide and so proposed a dissociative mechanism. For the cobalt compound all eight carbonyls exchanged, at the same rate, via a dissociative mechanism with a slightly higher energy of activation. With similar results being obtained for the lactone derivative $Co_2(CO)_7(C_7H_8O_2)$ the premise was only one bridging Co - C - Co bond need rupture to enable exchange. With other simple first row transition metal carbonyls exchange was much slower. Two mechanisms were proposed. Either



which implies free rotation about the cobalts in the active intermediates to explain the eight carbonyls all exchanging; or



In 1963 a series of papers by Bor and Noack finally resolved the dilemma. The X Ray determined structure of crystalline $Co_2(CO)_8$[88] confirmed the structure proposed by Mills and Robinson[86] (as shown in Fig. 1.13) except the bond angles deviate somewhat from C_{2v} symmetry resulting in the lower symmetry of C_S in which all vibrations are i.r. allowed

(six in the terminal region and two in the bonding region).

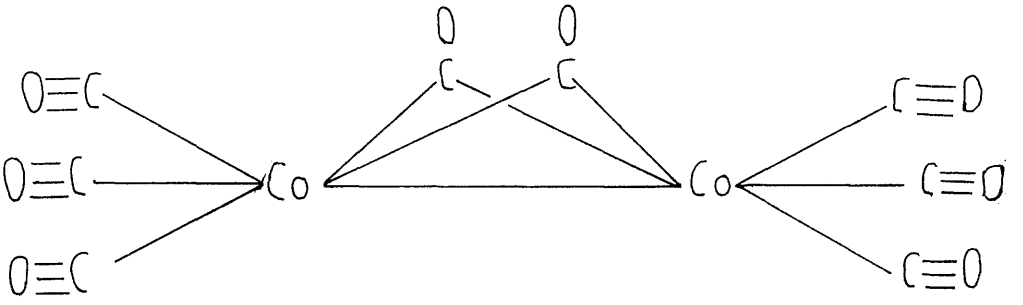


Figure 1.13

The cobalt atoms are linked by one bent M - M bond and two carbonyl bridges which are not in the same plane. However these results did not carry over to the solution i.r. spectrum of $Co_2(CO)_8$ [89]. It was established that the totally symmetric mode of vibration ν_1 was the highest i.r. absorption in the spectrum, although very weak, and the structure belonged to one of the asymmetric point groups C_n, C_{nv}, C_s or S_4.

Noack then performed a series of temperature experiments on solutions of $Co_2(CO)_8$ to test suggestions that there were different isomeric forms in equilibrium in solution[90]. In going from room temperature to -105°C there proved to be very pronounced changes in the i.r. absorption with two dependent isomers in co-existance. The low temperature form (L.T.F.) has bridging carbonyls while the high temperature form (H.T.F.) has none. The i.r. absorptions of the H.T.F. were 2069, 2031 and 2022 cm^{-1} (all terminal CO stretches) and the L.T.F. had values 2071, 2044 and 2042 cm^{-1} (terminal CO stretches), 1866 and 1857 cm^{-1} (bridging CO stretches). The L.T.F. was identified with the crystal structure of $Co_2(CO)_8$ because of the good agreement of i.r. data (expected $5\nu_{CO}$ terminal + $2\nu_{CO}$ bridging, found 3 strong terminal bands and 1 weak band at 2110 cm^{-1} [89], the other terminal band being one of the unassigned weak absorptions, and two bridging absorptions). The H.T.F. has three terminal ν_{CO} which decrease in intensity with decreasing temperature. Overall, at room temperature

the equilibrium of these two isomers favours the H.T.F. By molecular weight determinations this exists with M - M bonding and not as free $\cdot Co(CO)_4$ radicals. By comparison of its i.r., favourably, with mercury dicobalt octacarbonyl, $Hg[Co(CO)_4]_2$, a similar structure is suggested (Fig. 1.14 - $cf(OC)_4Co\text{-}Hg\text{-}Co(CO)_4$). This is assigned D_{3d} symmetry with three i.r. active carbonyl bands ($2A_{2u} + E_u$)

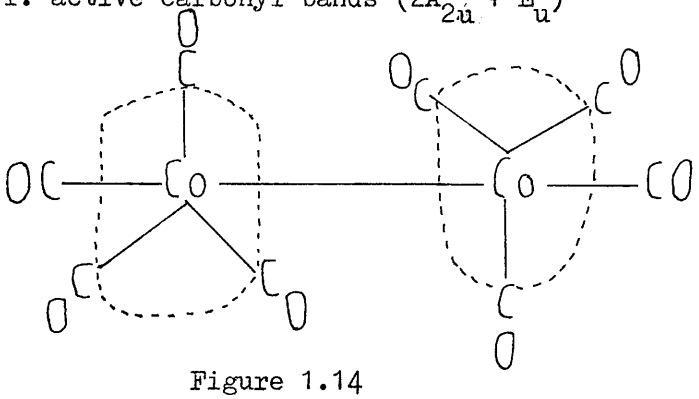


Figure 1.14

This is isoelectronic with $[Fe_2(CO)_8]^{2-}$ which has a linear structure with no carbonyl bridges and a metal - metal bond[91].

The second isomer is probably the intermediate in the rapid and equal carbon monoxide exchange of the eight carbonyl groups of $Co_2(CO)_8$, described by Basolo and Wojcicki[87].

Bor at the same time reached very similar conclusions by studying the i.r. spectrum and assigning all the modes of vibration[92]. He proposed a tetragonal pyramidal configuration about cobalt for the unbridged isomer with the carbonyl groups being eclipsed or staggered, his i.r. analysis preferring the former structure of C_{2v} symmetry (this would require seven i.r. active modes $3A_1 + 3B_1 + B_2$ as opposed to the eight i.r. active modes required by the staggered conformation). The stretching modes for the eclipsed conformation are detailed below in Fig. 1.15.

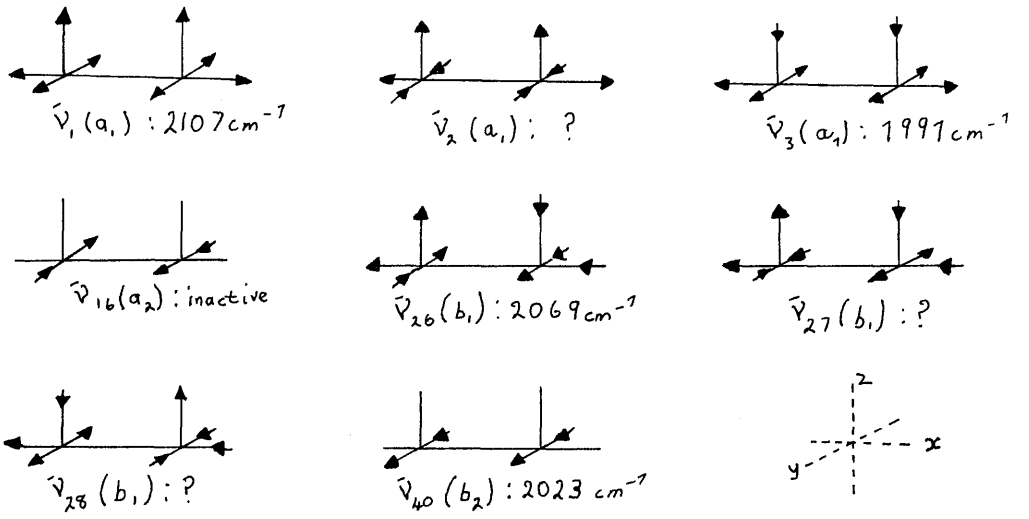


Figure 1.15

Bor concluded his paper by constructing a table assigning the observed i.r. frequencies to the different isomers - see Table 1.1.

Table 1.1

Assignment of the C-O stretching frequencies of $Co_2(CO)_8$ to the two isomers being present as equilibrium mixture in solution (wave numbers measured in hexane or heptane solution, $\pm$ 1 cm^{-1}).

$\bar{\nu}$ (CO)	Isomer	Normal Mode
2112	I	$\bar{\nu}_1$
2107	II	$\bar{\nu}_1$
2071	I	$\bar{\nu}_{26}$
2069	II	$\bar{\nu}_{26}$
2059	I (?)	
2044	*I	
2042	*I	
2031	I+II	$\bar{\nu}_2$ (I)
2023	II	$\bar{\nu}_{46}$
2001	I	$\bar{\nu}(^{13}C\text{-}O)$
1991	II	$\bar{\nu}_3$
1866	I	$\bar{\nu}_3$
1857	I	$\bar{\nu}_{28}$
1832	I	$\bar{\nu}(^{13}C\text{-}O)$

* low temperature work by Noack[90] was used to assign these absorptions.

Further work was carried out using a ^{13}CO enriched sample to resolve ambiguity of the weak bands[93]. This not only confirmed the existance of the second isomer but also indicated a third isomer of unknown structure. The conformation of the second isomer was shown to be the staggered conformation proposed earlier[90] and a tentative suggestion was made as to the conformation of the new isomer.

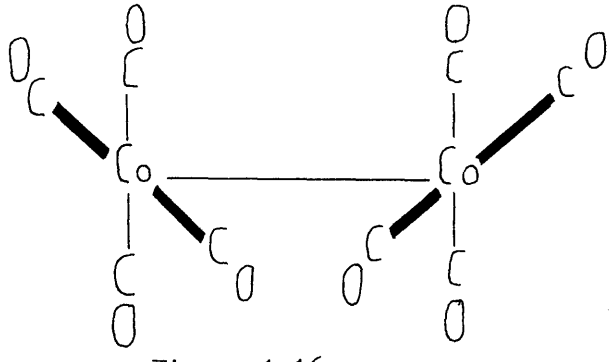


Figure 1.16

Raman spectroscopy confirmed the three tautomeric forms of $Co_2(CO)_8$ in solution[94] while electronic spectra showed the presence, at room temperature, of a 50:50 ratio of bridging : non bridging species (present as two or three isomers)[95].

$Co_2(CO)_9$ was still thought to exist; in 1970 its structure (inferred from the i.r. spectrum) was considered to be $[(OC)_4Co(CO)Co(CO)_4]$, related to the non bridged form of $Co_2(CO)_8$ [96a]. Later work assigned these i.r. signals to $HCo(CO)_4$, although the existence of $^{\bullet}Co(CO)_4$ or $^{\bullet}Co(CO)_5$ were not ruled out[96b]. Finally this compound was eliminated when evidence of a third isomer of $Co_2(CO)_8$ came to print. A high temperature i.r. study from -165 to +210°C was undertaken to furnish proof for this isomer[96c] and the band at 2031 cm^{-1} was assigned to it. The temperature dependence of $Co_2(CO)_8$ was represented by the sequence

form (I) $\rightleftharpoons$ form (II) $\rightleftharpoons$ form (III) increasing temperature $\longrightarrow$

Further evidence was elicited from matrix isolation work which intensified the absorptions for isomer III by a factor of four w.r.t. other absorptions[97]. The various assignments are tabulated below.

Table 1.2

Freq in Ar matrix, cm^{-1} [a,b]	Assignment	Freq in hexane soln, cm^{-1}	Assignment
2117(0.1)	I[c]	2111.8	I
		2107.2	I
2076.4(10.0)	I	2071.0	I
2073.5(4.3)	II	2068.8	II
2059.2(5.2)	III	2058.6	III
2051.5(1.9)	II[d]		
2050.1(1.9)	I[d]	2044.0	I
2047.6(7.8)	I[d]	2042.4	I
2042.8(1.8)	III[d]		
2035.3(7.0) }	III	2030.7	I + II
2032.3(4.9) }			
2029.8(7.3) }	II	2022.7	II
2025.7(4.8) }			
2021.7(0.7)	?		
2007.1(0.4)	I(^{13}CO)	2001.7	I(^{13}CO)
2006.4(0.6)	III(^{13}CO)		
2002.1(1.4) }	III	1991.0	III
1996.4(2.0) }			
1867.9(2.7)	I	1866.0	I
1857.4(4.2)	I	1857.2	I

[a]Numbers in parentheses are relative integrated intensities taken from spectra resolved by curve fitting. [b]Bands thought to be split by matrix effects are indicated by braces. [c]Assignment to a particular isomer is in doubt because of low intensity of the band. [d]Assignment in doubt because of severe overlapping of bands.

The third isomer was reckoned to account for as much as 30% of $Co_2(CO)_8$ at room temperature and dominates at higher temperatures. It gives rise to four bands in the i.r. plus a ^{13}CO isotope band. There are no bridging carbonyls in the molecule, although four different conformations are possible for a non bridged species (Fig. 1.17).

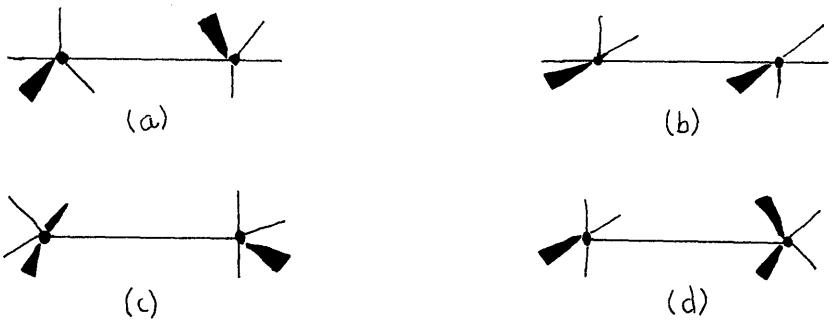


Figure 1.17 - Possible structures of isomer 3.

The theoretical i.r. signals are tabled below.

Table 1.3

Isomer	Symmetry	Modes	
		i.r. active	i.r. inactive
a	D_{3d}	$2A_{2u} + E_u$	$2A_{ig} + E_g$
b	C_{2h}	$2Au + 3B_u$	$3Ag + B_g$
c	D_{2d}	$2B_2 + 2E$	$2A_1$
d	D_{4d}	$B_2 + E_1$	$A_1 + E_2 + E_3$

(a) was assigned to isomer I, (d) was eliminated because it could not give rise to enough i.r. signals. Of the two remaining possibilities, the authors favoured (c).

The existence of a fourth isomer, with one $Co(CO)_4$ group in an axial position and the other in a radical position (shown in Fig. 1.18) has been postulated[98] but substantiating evidence has not been forthcoming.

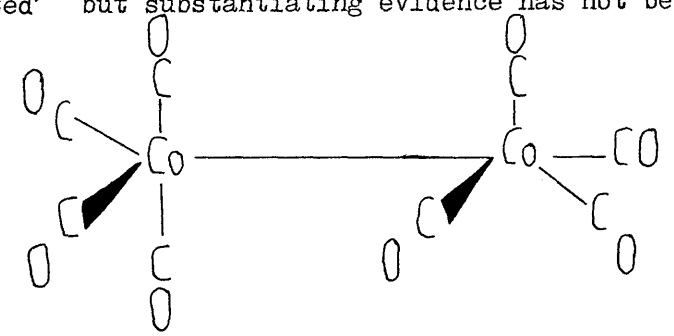


Figure 1.18

Tetracobalt dodecacarbonyl, $Co_4(CO)_{12}$, also has a long history. Corradini[99a] studied the crystalline structure and summarised his results:

1. There is an approximately regular tetrahedron of cobalt atoms.
2. The molecules are disordered, making it impossible, with the data available, to specify accurately the arrangement of the carbonyl groups.
3. The most likely arrangement of the carbonyl groups for the molecule in the crystal is one in which one cobalt atom is bound to three terminal carbonyl groups while the other cobalt atoms are each bound to two terminal carbonyl groups with the three edges between them being spanned by bridging carbonyl groups. This structure would possess idealised C_{3v} symmetry.

However, i.r. spectra (in pentane) did not bear this out. The solution i.r. indicates four bridging carbonyl groups and two terminal groups on each cobalt to give D_{2d} symmetry[99b].

It was pointed out that these facts were not necessarily incompatible[100], but that the two structures could interconvert, via a tetrahedral intermediate containing only terminal carbonyl groups on going from solid to solution phase.

More recently, Johnson & Benfield have reviewed the conflicting reports and new evidence from isotopic i.r. studies and Raman spectra[101]. They concluded that the solid structure has C_{3v} symmetry (with crystal disorder) involving a tetrahedron of cobalt atoms in an icosohedron of carbonyls, the disorder being caused by different orientations of the cobalt atoms. In solution, isotopic studies favour a structure of C_{3v} symmetry, as does the ^{59}Co n.m.r. spectrum of $Co_4(CO)_{12}$. ^{13}C i.r. isotopic studies appear to confirm Cotton's mechanism of exchange[100], although there was still some doubt. Carbonyl scrambling was now thought to be a single type of process via a cubo-octohedran transition

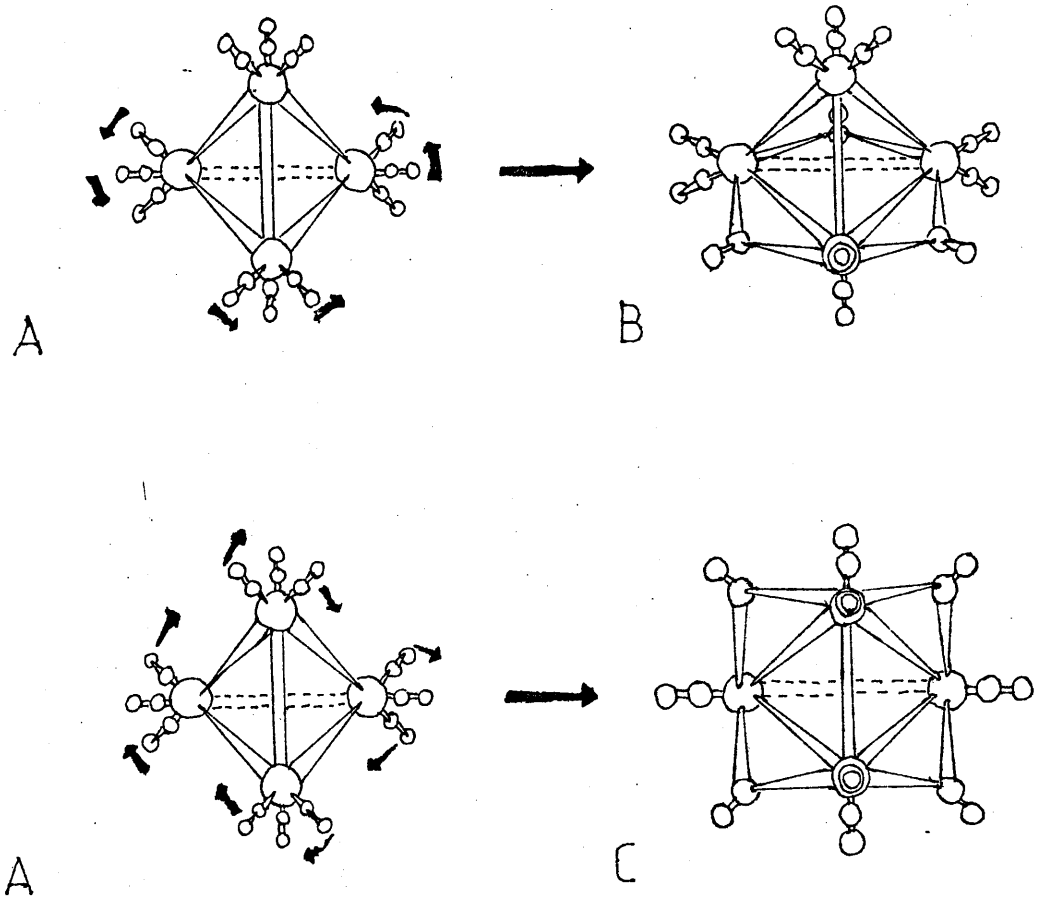


Figure 1.19

state. Different patterns of carbonyl scrambling were a consequence of the geometric disposition of the metal atom tetrahedron within the ligand polyhedron.

Cobalt carbonyl derivatives undergo varied numbers and types of reaction, one of the most important being the "CO insertion" reaction. This and other synthesis and reactions of alkylcobalt and acylcobalt tetracarbonyls have been extensively reviewed[102].

The first simple alkylcobalt compound of any kind, $MeCo(CO)_4$, was prepared, naturally, by Hieber et al.[103], and proved to be a yellow air sensitive derivative.

$$MeI + NaCo(CO)_4 \longrightarrow MeCo(CO)_4 + NaI \qquad (1.23)$$

This method can be used for other alkylcobalt tetracarbonyls although yields are poor.

A second method involves the addition of cobalt hydrido-tetracarbonyl to olefins[104], while a third route involves $HCo(CO)_4$ and epoxides which react to evolve 2 - hydroxyalkylcobalt tetracarbonyl derivatives.[105].

For acylcobalt tetracarbonyl there are two general methods[106]

a) $$RCOX + [Co(CO)_4]^- \longrightarrow RCOCo(CO)_4 + X^- \qquad (1.24)$$

b) $$RCo(CO)_4 + CO \rightleftharpoons RCOCo(CO)_4 \qquad (1.25)$$

The latter is a reversible reaction with the equilibrium lying far to the right hand side. These species tend to be more stable than the corresponding alkyl derivatives. Both classes of compounds can undergo ligand replacement reactions (straight substitution for acyl compounds, CO insertion and substitution for alkyl compounds) or substitution to form chelates[106] as depicted in Fig. 1.20. e.g.

$$EtOCOCH_2Br + NaCo(CO)_4 \longrightarrow EtOCOCH_2Co(CO)_4$$

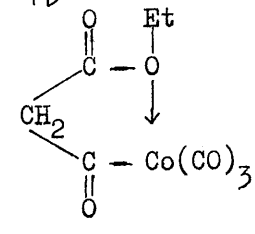


Figure 1.20

They will undergo Co – C cleavage reactions[107] e.g. alcoholysis and ammonolysis e.g.

$$RCOCo(CO)_4 + R'OH \longrightarrow RCOOR' + HCo(CO)_4 \qquad (1.26)$$

or reductive cleavage (of acylcobalt carbonyls)[108] e.g.

$$MeCOCo(CO)_4 + H_2 \longrightarrow MeCHO + HCo(CO)_4 \qquad (1.27)$$

This reduction is likely to be the last step in the Oxo reaction.

Thermal decomposition of alkylcobalt tetracarbonyl leads to the corresponding acylcobalt tetracarbonyl[109] probably via disproportionation.

$$2RCo(CO)_4 \rightleftharpoons RCOCo(CO)_4 + RCo(CO)_3 \qquad (1.28)$$

This can undergo further reaction.

Insertion reactions with carbon monoxide, olefins and acetylenes have all been observed, where insertion is taken to indicate the nature of product formed. With carbon monoxide insertion into the alkylcobalt tetracarbonyl to form the acyl species, the mechanism is believed to involve a 1:2 shift of the alkyl group from Co to C followed by reaction of this intermediate with another external carbon monoxide molecule. Finally these species can themselves insert into certain unsaturated carbonyl systems[110].

$$CH_2=CH-\overset{R}{\underset{|}{C}}=O + R'Co(CO)_4 \longrightarrow HC\begin{array}{l}\diagup\ \overset{OCOR'}{\overset{|}{C}}-R \\ \diagdown\ \underset{H_2}{C}\end{array}Co(CO)_3 \qquad (1.29)$$

$R = CH_3$ or H

Acylcobalt carbonyl species have also been synthesised by phase transfer and three phase catalysis using RCH_2X and $[Co(CO)_4]^-$ [111] and stable alkylcobalt carbonyl complexes of general formula $ROOCCH_2Co(CO)_3L$ have been prepared[112]. An important role of these compounds is as intermediates in catalytic reactions.

Metal carbonyls have been involved in a host of organic synthesis e.g. carbonylation of organic halides to the corresponding acetic acid[113],

initiating reactions between organic halides and olefins or acetylenes[114], as well as being used as reagents in organic preparative chemistry[115]. The specific use of cobalt carbonyls in such roles has been reviewed[76,116].

The Oxo, or hydroformylation process, has long been in use. This is the method of converting olefins into aldehydes. i.e.

$$RCH=CH_2 + CO + H_2 \xrightarrow{\text{catalyst}} RCH_2CH_2CHO \qquad (1.30)$$

$$C_n \text{ olefin} \longrightarrow C_{n+1} \text{ aldehyde}$$

The active catalyst is $HCo(CO)_4$[117] but as this reaction is carried out at high pressure (200-300 atmospheres) and temperatures between 100-120°C any cobalt carbonyl compound can be used as the catalyst since it will be converted to $HCo(CO)_4$ under these conditions. The high temperatures are needed to alleviate the carbon monoxide poisoning (which occurs at the high pressures) but between 150-200°C the reduction of the aldehyde to a primary alcohol occurs. The presence of phosphorus at these temperatures will stimulate this secondary reaction.

The probable mechanism for hydroformylation is outlined in the scheme below:

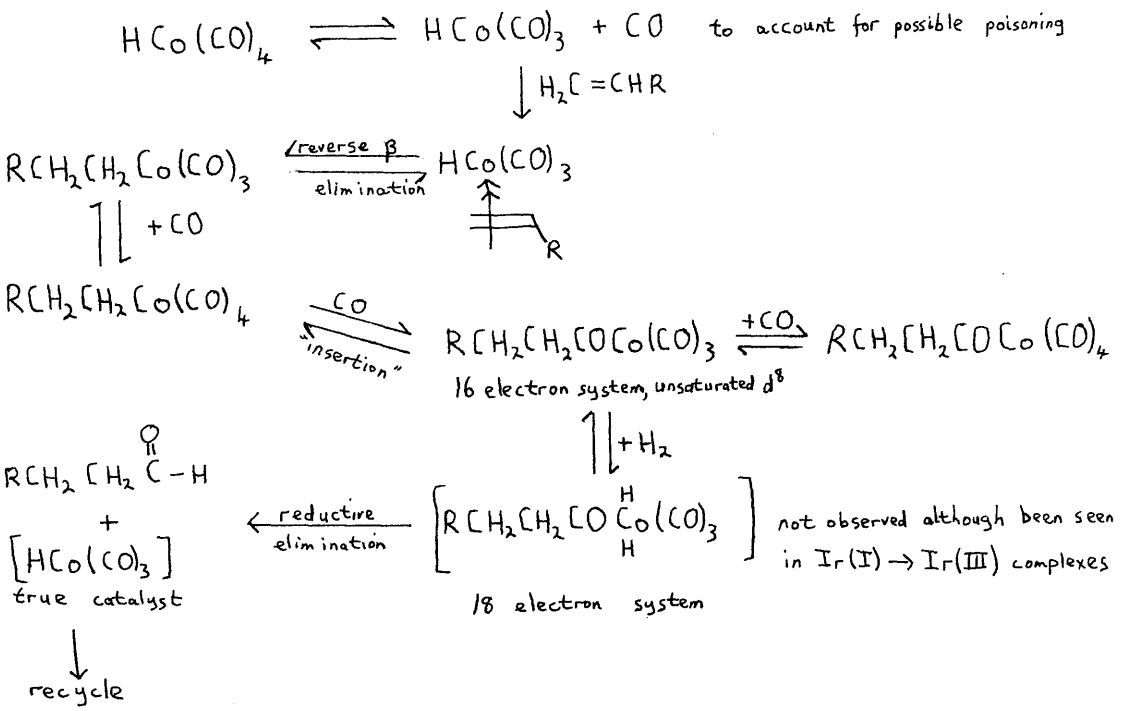
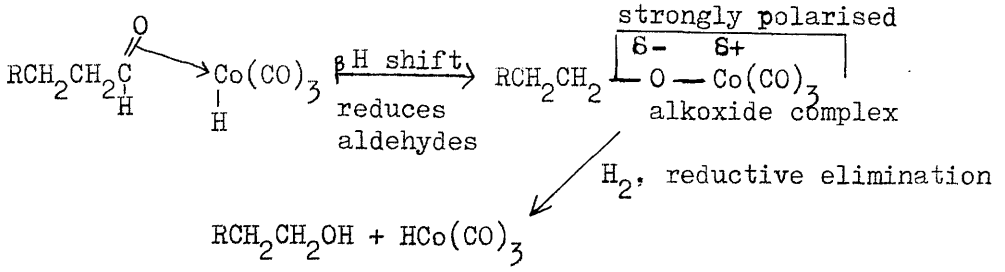


Figure 1.21

For the alcohol cycle the scheme in Fig. 1.22 would apply:



$$RCH_2CH_2OH + HCo(CO)_3$$

Figure 1.22

Phosphines will favour this reaction because $Co(CO)_2PR_3$ will be less electronegative than $HCo(CO)_3$ species and any reduction in electron density at the metal will favour the β H shift. Evidence of this mechanism has come from matrix isolation i.r. studies of $HCo(CO)_4$. In a low temperature argon matrix, a weak band at 2018 cm^{-1} was observed. On irradiation this grew along with production of some new bands which were then assigned to $HCo(CO)_3$, a coordinately unsaturated species. No evidence for this species, the olefin complex or the alkylcobalt carbonyl complex has been obtained directly[118].

There are variants on the Oxo process. Carbonylation of an alcohol to an acid can occur when an alcohol is the starting material.

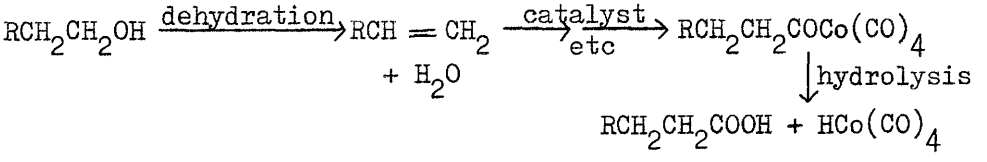


Figure 1.23

The problem with this synthesis is dehydration of the alcohol is often not clean.

An easy preparative method for $C_2H_5COC_2H_5$ is to use ethylene in a deficiency of hydrogen

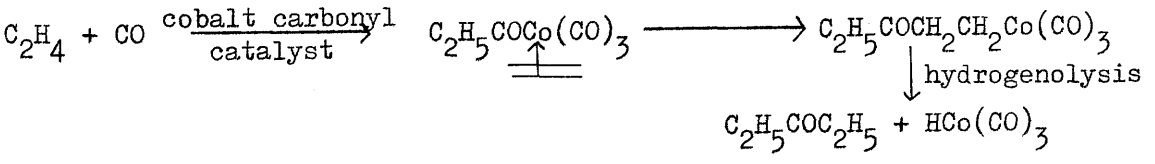
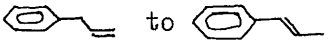


Figure 1.24

As already stated benzyl halides will react with $[Co(CO)_4]^-$ to give the intermediate $PhCH_2Co(CO)_4$ which on treatment with carbon monoxide, methanol and base (to mop up H^+) will give $PhCH_2COOCH_3$ + $[Co(CO)_4]^- + H^+$. Cobalt carbonyls have a tendency to initiate formation of secondary alkyls and secondary carbonylated species in hydroformyation and so present day techniques employ iridium or rhodium as the catalyst because they favour terminal carbonylated species.

The Woodward - Hoffman direct rearrangement of  to (1,3 supra H shift) is forbidden but the process has been made possible using $HCo(CO)_4$. The method is outlined in Fig. 1.25.

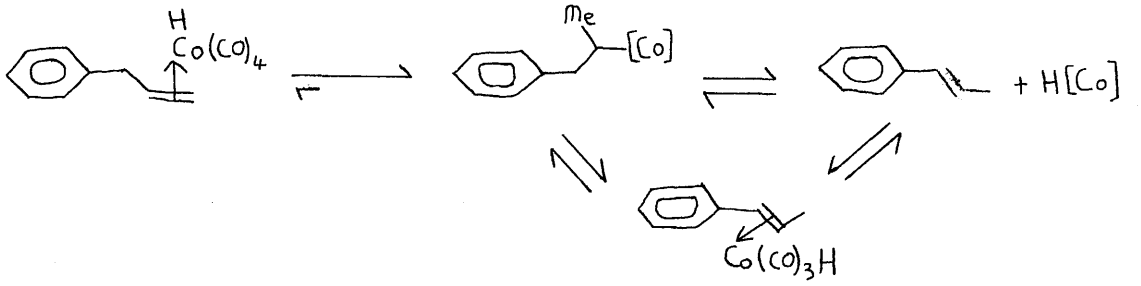


Figure 1.25

This one aspect of catalytic behaviour has been updated recently by comparing the efficiency of Rh and Co catalysts in the hydroformylation of olefins[119].

The hydroformylation of formaldehyde to glycolaldehyde, in high yield, can be achieved using $HCo(CO)_4$ at 0°C (equation 1.31)[120].

$$CH_2O + HCo(CO)_4 \xrightarrow[0^\circ C,\ CH_2Cl_2]{CO,\ 1\ atm} HOCH_2CHO \qquad (1.31)$$

showing that high pressure and temperatures are no longer required for such synthesis. The catalytic step seems to be bonding by Co - C as opposed to Co - O bonding.

Dicobalt octacarbonyl was one of the earliest compounds believed to be capable of activating molecular hydrogen in homogeneous solutions and has been used widely in the reduction of olefins and aldehydes. Its hydride $HCo(CO)_4$ has been used in isomerisation reactions particularly

of olefins and this topic has been reviewed[122].

Substitution reactions involving $Co_2(CO)_8$ have received much attention. One such reaction involves phosphines[123]. When a 1:2 mole ratio of $Co_2(CO)_8$: Ph_3P in hexane react, the solid salt $[Ph_3PCo(CO)_3PPh_3]^+$ $[Co(CO)_4]^-$ was isolated. On heating in toluene further reaction to the dimer $[Ph_3PCo(CO)_3]_2$ occurs.

The kinetics of the reaction were determined at -72°C and the substitution was found to occur in three distinct stages[8]

1. $Co_2(CO)_8 + PPh_3 \longrightarrow Co_2(CO)_8PPh_3$
2. $Co_2(CO)_8PPh_3 \longrightarrow Co_2(CO)_7PPh_3 + CO$
3. $Co_2(CO)_7PPh_3 + PPh_3 \longrightarrow [Co(CO)_3(PPh_3)_2]^+ [Co(CO)_4]^-$

The initial step of forming $Ph_3P\ \overset{\delta+}{Co}(CO)_3 - \overset{\delta-}{Co}(CO)_4$ is fast and the final step is so fast at room temperature that the intermediate is not observed.

Kinetic studies of AR_3 compounds (A = P, As, R =Ph, Bu) substituting in $Co_2(CO)_8$ shows that different products are obtained[124]. The phosphorus ligands react to form $[Co(CO)_3(PR_3)_2]$ $[Co(CO)_4]$ whereas $AsPh_3$ gives the substituted product $Co_2(CO)_6(AsPh_3)_2$ via the intermediate $Co_2(CO)_7AsPh_3$. This is thought to involve a radical chain mechanism, the key steps of which are outlined in Fig. 1.26.

$$Co(CO)_3L + Co_2(CO)_8 \longrightarrow Co(CO)_3L^+ + [Co_2(CO)_8]^- \xrightarrow{\text{dissociation}} [Co(CO)_4]^- + Co(CO)_4$$
$$\downarrow L$$
$$Co(CO)_3L^{\cdot}$$

Figure 1.26

Earlier work had shown that η^5-$C_5H_5Co(CO)_2$ in T.H.F. under air and water free conditions and at room temperature gave $NaCo(CO)_4$ and the radical species $Na^+[(\eta^5\text{-}C_5H_5)_2Co_2(CO)_2]^-$[125]. With the $^{\cdot}Co(CO)_4$ radical itself known since the sixties[105], the above mechanism is not creating imaginary species.

The proof of radical cobalt carbonyl species has come from matrix isolation work. $HCo(CO)_4$ in both argon and carbon monoxide matrices showed evidence of M - H bond cleavage[126] i.e.

$$HCo(CO)_4 \xrightarrow{h\nu} H^{\cdot} + {}^{\cdot}Co(CO)_4 \qquad (1.32)$$

which led to the reassignment of the $HCo(CO)_3$ species postulated earlier[118]. Ungváry and Markó showed that the thermal decomposition of $HCo(CO)_4$ in solution to give $Co_2(CO)_8 + H_2$ proceeds via the ${}^{\cdot}Co(CO)_4$ radical[127]. The mechanism for photochemical decay of $HCo(CO)_4$ to $Co_2(CO)_8$ has been derived[128] as set out below:

$$Co_2(CO)_8 \rightleftharpoons 2Co(CO)_4^{\cdot}$$

$$Co(CO)_4^{\cdot} \rightleftharpoons Co(CO)_3 + CO$$

$$Co(CO)_3 + HCo(CO)_4 \rightleftharpoons HCo_2(CO)_7^{\cdot}$$

$$HCo_2(CO)_7^{\cdot} + HCo(CO)_4 \longrightarrow H_2Co_2(CO)_7 + Co(CO)_4^{\cdot}$$

$$H_2Co_2(CO)_7 \longrightarrow H_2 + Co_2(CO)_7$$

$$Co_2(CO)_7 + CO \longrightarrow Co_2(CO)_8$$

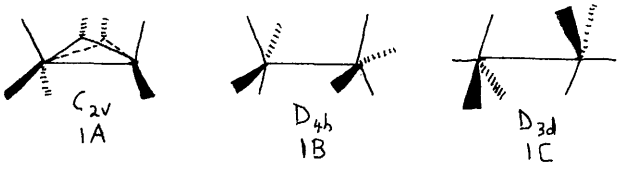
Figure 1.27

Radicals are involved in the mechanism of substitution in $Co_2(CO)_8$ [129] When L = PBu_3, the compound obtained is $[Co(CO)_3L_2][Co(CO)_4]$. With stop flow kinetics the mechanism operating was shown to involve a radical chain mechanism including an outer sphere electron transfer from $Co(CO)_3L^{\cdot}$ radical to $Co_2(CO)_8$ (c.f. ref. 8).

Other cobalt carbonyl entities have been given life by matrix isolation techniques. $Co_2(CO)_7$ has long been regarded as an intermediate in the reactions of $Co_2(CO)_8$ e.g. in hydroformylation. It was established by photochemical decompostiion of $Co_2(CO)_8$ in an argon matrix[130], and shown to possess no bridging carbonyls. ${}^{\cdot}Co(CO)_4$ radicals co-exist with $Co_2(CO)_7$ in the carbon monoxide matrix along with a secondary decomposition product tentatively assigned as $Co_2(CO)_6$.

Even theoretical calculations have been brought to bear on this topic. A paper detailing Extended Huckel Theory Calculations on the various cobalt carbonyl species involved in hydroformylation (viz. $Co_2(CO)_8$,

$Co_2(CO)_7$, $^{\cdot}Co(CO)_4$ and $Co(CO)_3$) has been published[131a], deriving the geometries of the stable isomers and interpretating the i.r. spectrum of $Co_2(CO)_8$. The stable geometries were considered to be:

$Co_2(CO)_8$ 

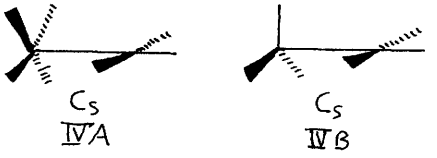
(C_{2h} and D_{2d} symmetries being discounted as unstable)

$Co(CO)_4$ 

(C_{3v} isomer considered unstable by EHT calculation)

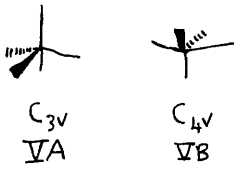
$Co(CO)_3$ 

(Both C_{3v} and C_{2v} isomers considered unstable by EHT calculation)

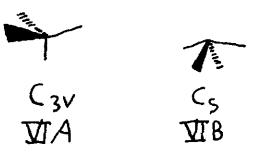
$Co_2(CO)_7$ 

(Both C_s [] and C_{3v} isomers considered unstable by EHT calculation)

Isomer A is more stable than isomer B.

$HCo(CO)_4$ 

(C_{3v} has been established by experimental results, while C_{4v} isomer is predicted by EHT calculation)

$HCo(CO)_3$ 

(C_{3v} structure favoured by earlier work although EHT calculation predicts C_s structure as the more stable)

Figure 1.28

$Co_2(CO)_7$ has been proposed as an intermediate in the reactions[132] :

$$Co_2(CO)_8 + H_2 \rightleftharpoons 2HCo(CO)_4 \qquad (1.33)$$

$$2Co_2(CO)_8 \rightleftharpoons Co_4(CO)_{12} + 4CO \qquad (1.34)$$

This gives a pathway for dissociation of $Co_2(CO)_8$ as follows:[131a]

$$\begin{array}{ccc} Co_2(CO)_8\ (IB) & \xrightarrow{1b} & 2Co(CO)_4\ (IIA) \\ 1a \downarrow -CO & & -CO \downarrow 2b \\ Co_2(CO)_7\ (IVA) & \xrightarrow{2a} & {}^{\bullet}Co(CO)_4 + {}^{\bullet}Co(CO)_3\ (IIIA) \end{array}$$

Figure 1.29

${}^{\bullet}Co(CO)_4$ radicals recombine with high efficiency[130] and this would favour the route 1a - 2a. The stable isomers of $HCo(CO)_3$ could also account for the complex which it appears to form with the olefin in the Oxo process.

Further Extended Huckel Calculations have been conducted to investigate the influence of substitution on the structure of $Co_2(CO)_8$ [131b]. Using ethylene, cis-butadiene and cyclopentadienyl anion as substituents the geometries of the eclipsed and staggered forms of $Co_2(CO)_8$ were calculated and the former was found to be in the form of a puckered ring (i.e. two cobalts plus the two bridging carbonyls) and the latter to be planar and lower in energy by 20.12 kcal mol^{-1}. The replacement of two, four or six carbonyls by two ethylenes, cis-butadienes, or cyclopentadiene anions gives tautomers with the inner ring planar in the trans isomer while puckered in the cis isomer. The magnitude of the flap angle depends on the nature of the substituents, not the number of replaced carbonyls. Cis/trans isomerisation, by analogy to the isomers of $Co_2(CO)_8$, will occur through ring opening with the intermediates being of the open form for $Co_2(CO)_8$ and its substituted derivatives.

The other main class of cobalt carbonyl compounds is the anionic species, a few of which are detailed below.

One of the most important is $[Co(CO)_4]^-$ which is active in many catalytic reactions. As much of the work to be discussed involves this anion, only a short account will be given here.

The anion is formed in many ways, usually by disproportionation of $Co_2(CO)_8$. This can be achieved using bases or more recently by halides. The general equation is:

$$3Co_2(CO)_8 + 4X^- \rightleftharpoons 4[Co(CO)_4]^- + 2Co^{2+}X_2 + 8CO \qquad (1.35)$$

Its i.r. spectrum has suffered a great deal of attention, especially by Edgell and his co-workers, showing the effects of solvent on band shape and the different types of contact ion pairs which can be found. Another anion which has recently enjoyed great popularity is $[Co_3(CO)_{10}]^-$. Its prominence is due to the attention given to it by Fachinetti and his team who have determined the crystal structure of its Li^+ salt (which is very air sensitive) and have shown the effects of carbon monoxide on the very delicately balanced equilibrium between $[Co(CO)_4]^-$, $Co_2(CO)_8$ and $[Co_3(CO)_{10}]^-$. This aspect will be dealt with later at greater length (chapter 3).

$[MCo(CO)_9]^-$ (from $[M_2(CO)_{10}]^{2-}$ and $Co_2(CO)_8$, M = Cr,W) and $[FeCo(CO)_8]^-$ (from $Fe(CO)_5$ and $[Co(CO)_4]^-$) have been noted[133] with the latter having a structure similar to the bridged isomer of $Co_2(CO)_8$ (by i.r. studies).

The anions $[Co_6(CO)_{14}]^{4-}$ and $[Co_6(CO)_{15}]^{2-}$ and the neutral $[Co_6(CO)_{16}]^{o}$ are well documented. The first ion is prepared from the reduction of $Co_4(CO)_{12}$ by an alkali metal in T.H.F. and its structure has been determined[134] showing an octahedral cluster of metal atoms surrounded by fourteen carbonyl groups (six terminal, and eight triply bridging). $Co_6(CO)_{16}$ was prepared using mild oxidising reagents with an aqueous solution of $[Co_6(CO)_{14}]^{4-}$ or $[Co_6(CO)_{15}]^{2-}$, giving black, air sensitive crystals[135]. The dinegative anion was initially

synthesised from an ethanol solution of $Co_2(CO)_8$ heated to 60°C (if T.H.F. or other solvents are used at this temperature $Co_4(CO)_{12}$ results); alternatively $[Co(CO)_4]^-$ can be refluxed, in vacuo, at 60°C to give a solution of $3[CoB_6][Co_6(CO)_{15}]$[136] (B = Lewis base). Its i.r. spectrum shows it to be an intermediate structure between $Co_2(CO)_8$ and $[Co(CO)_4]^-$ derivatives and it is only stable in the absence of free base[134]. Protonation of the anion gives the interstitual compound $[HCo_6(CO)_{15}]^-$ which has the hydrogen bound to the six metal atoms[137], accounting for the very unusual δ value of the complex (23.2 ppm, where for normal hydrides δ ranges between 0 and -40 ppm). The proton is mobile and at high temperatures can leave the cluster and exchange with the solvent. The structure determination of this compound showed the value of characterising complexes by X Ray and neutron diffraction. The former showed the compound to have one very long M - M bond with attendant carbonyl groups moving away from the metals, suggesting an edge bridging M - H - M system. Neutron diffraction however pinpointed the hydrogen atom to be in the centre of the octahedron of metals and bound to each of them; the long M - M bond was solely due to steric effects of the carbonyls. Similar effects have been found in the corresponding ruthenium complex. The possibility of four or five coordinate hydrogen in the systems $[H_2Rh_{13}(CO)_{24}]^{3-}$ and $[H_3Rh_{13}(CO)_{24}]^{2-}$ has been suggested but not yet proven. This would complete the sequence of coordination numbers for hydrogen; at present examples of 1, 2, 3 and 6 coordinated hydrogen have been found.

The hydride, $HCo(CO)_4$ is relatively simple to synthesise (cobalt, carbon monoxide and hydrogen under pressure) and is acidic in nature ($pK_a \sim 1$ in water)[138] so that although it is very toxic, it can easily be destroyed in alkaline solutions or by air oxidation. Hieber has prepared the more stable phosphorus substituted derivatives, $HCo(CO)_{4-n}L_n$ (n = 1,2 and

L = Ph_3P, $P(OPh)_3$ etc.) and found them to be considerably less acidic[139]. Halide derivatives of cobalt carbonyls have been made, but these are only stable at low temperatures[140]. In hydrocarbon solution, at -40°C, they have the general formula $Co(CO)_4X$, X = I, Br, Cl, although the solid cannot be isolated. From their i.r. spectra the compounds seem to be trigonal bipyramidal with C_{3v} symmetry ($2A_1$ + E i.r. active modes of vibration). The more stable phosphine substituted compounds $Co(CO)_3(PR)_3X$ and $Co(CO)_2(PR_3)_2$ have been investigated[141], their decomposition pathways explaining the catalytic action of iodine in the high pressure synthesis of $Co_2(CO)_8$ - the initial formation of $CoI_2(CO)$ is now thought to convert to $Co_2(CO)_8$ and CoI_2 via the labile $Co(CO)_4I$ intermediate.

One last branch of cobalt carbonyl chemistry which should be briefly mentioned is compounds of the type $M[Co(CO)_4]_2$ (M = Cd, Zn, Hg or Sn) and $M[Co(CO)_4]_3$ (M = In, Tl). These initially were formed during the attempted preparation of metal carbonyls from cobalt halides using another metal as the halogen acceptor[142].

$$2CoBr_2 + 3Zn + 8\ CO \xrightarrow[350\ atm]{200^\circ C} Zn[Co(CO)_4]_2 + 2ZnBr_2 \qquad (1.36)$$

The mercury salt is even easier to prepare:

$$HgX_2 + 3Co + 8CO \xrightarrow[200\ atm]{150^\circ C} Hg[Co(CO)_4]_2 + CoX_2 \quad X = Br, I \qquad (1.37)$$

This will undergo $Co_2(CO)_8$ type substitution reactions to give compounds of $Hg[Co(CO)_3L]_2$ which will be discussed in chapter 4.

In recent years many other mixed metal compounds containing cobalt and carbon monoxide have been prepared, especially Ge and Sn clusters. Exploration into cluster chemistry in an effort to understand the reactions of gross metals has become popular. This is because compounds such as $Co_3(CO)_9(\mu_3X)$, where X = CCH_3 or $COBCl_2NEt_3$ type ligands, can be regarded as a Co_3X cluster or a piece of metal containing three cobalts with a substrate X stuck on to the side.

One of the most valuable tools in carbonyl chemistry is the infrared form of vibration spectroscopy. Metal carbonyls have very strong carbonyl stretches in the 2200 - 1700 cm^{-1} region which are extremely sensitive to metal centre, effects of other ligands in the molecule and the interaction of outside influences e.g. solvent. The number and pattern of the absorption bands, together with their position can be interpreted to give an insight into the symmetry of the molecule, its environment and its bonding. The idea that the number of i.r. bands observed is related to the local symmetry of the molecule has been known for some time[143].

The symmetry of the isolated carbon monoxide molecule is $C_{\infty v}$ but on coordination this is drastically lowered. Local symmetry is maintained during a bond stretching vibration, which means mixing of the in-phase with the out-of-phase π orbitals cannot occur. The relative charge densities on the atoms of a coordinated carbon monoxide group is $\delta^+ - \delta^-$ (as shown by ab initio calculations on $Ni(CO)_4$ which also suggests that both the carbon and oxygen atoms carry small residual negative charges[144]). If the bond of a coordinated carbon monoxide group is stretched the probable reaction is to transfer electron density from carbon to oxygen[145]. When this occurs in the area of the π system the "empty" π^* orbitals of the carbonyl group will be lowered in energy and become more localised on the carbon atom, leading to enhanced M$\longrightarrow$C π electron donation i.e. bonding. An alternative approach is to replace the carbonyl ligands attached to a metal by more powerful σ donor (and poorer π acceptor ability) ligands. This reduces the effective nuclear charge of the metal while increasing the d orbital energy and size, which in turn leads to an enhancement of the M - C π bonding for the remaining carbonyl ligands. This weakens the carbonyl bond and so a smaller bond stretching force constant results.

Similar arguments show that highly electronegative groups (e.g. halogens) or increased effective nuclear charge on the metal means higher carbonyl stretching frequencies, relative to the parent complex.

The observed i.r. spectrum of a molecule has very close theoretical links. From group theory arguments, for any molecule, the number of vibrational degrees of freedom is equal to 3N - 6 (or 3N - 5 for a linear molecule for which only two rotational modes exist) where N is the number of atoms in a molecule. The six degrees of freedom that are eliminated are the three translational modes and the three rotational modes. Using the point group and symmetry properties of a molecule the character table can be constructed. From this the number of irreducible representations which span a particular point group is calculated and the six vibrational modes to be eliminated are removed. The vibrational modes which are left are then assigned as i.r. active, Raman active, or inactive according to whether they have a dipole moment (i.e. at least one of the x, y, z components is non zero) or an electronic polarizability (i.e. at least one of the α_{ab} components is non zero, a, b, $\in$ x, y, z) or neither of these apply.

It is found that a common group of atoms, i.e. a functional group, will absorb over a narrow range of frequencies, called the group frequency, no matter what other atoms may be present in the molecule[146]. This group frequency can be used to identify the functional groups in a structure e.g. methyl groups absorb in 3000 - 2060, 1470 - 1400, 1380 - 1200 and 1200 - 800 cm^{-1} regions, organic carbonyls (ketones etc.) absorb in the range 1800 - 1500 cm^{-1} while inorganic carbonyls absorb in the 2100 - 1750 cm^{-1} region.

Metal carbonyls themselves are classified as four groups:

a) Mononuclear carbonyls. Relatively simple case with the symmetry usually T_d (one i.r. active mode), O_h (one i.r. active mode) or D_{3h}

(two i.r. active modes).

b) Carbonyl Hydrides.

c) Substituted metal carbonyls.

d) Polynuclear carbonyls. In general the i.r. spectrum is split into two regions - terminal carbonyls and bridging carbonyls. Bridging carbonyls in general coordinate to both metal atoms through the carbon, either symmetrically or asymmetrically. Possible structures are shown below[147].

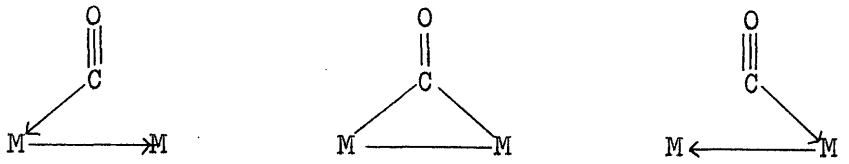


Figure 1.30

In asymmetrically bridging (a) and (c) of Fig. 1.30 contribute to different extents. There are a variety of possible arrangements of equivalent bridging carbonyl groups some of which are listed below.

2 groups Theory is similar to $M(CO)_2$ case - i.e. if both groups are equivalent, the group belongs to $C_{\infty v}$, C_{2v}, C_s or D_{3h} point groups. Should the bridging carbonyls be coplanar, the symmetric stretch will be vanishingly weak but it is formally allowed unless the complex is a member of a point group that includes C_i, S_u, D_u. It is always Raman allowed. The asymmetric stretch is i.r. allowed and intense but Raman forbidden for groups of symmetry C_i, D_n $(n \geqslant 3)$ or S_n $(n \geqslant 6)$; the selection rules depending on whether or not the groups are connected by a centre of symmetry.

3 groups Theory is similar to $M(CO)_3$ case - i.e. if all carbonyl groups are equivalent, the molecule belongs to point group C_3 or higher symmetry (often C_{3v}). The intensity of the A_1 mode vanishes when the three oscillating dipoles are coplanar. For D_{3h} the A_1 mode is i.r. forbidden,

the E mode is i.r. allowed and both are Raman allowed; point groups include C_{3v} and D_{3h}.

4 groups Theory is similar to $M(CO)_4$ case i.e. point group Td, spanned by A_1 and T_2 which are both Raman active with T_2 being i.r. active; point group is Td or compressed Td (point group D_{2d}) which has A_1, B_2 and E Raman active (E is small) and B_2 i.r. active.

8 groups Point group is S_6 and ideally Oh. For Oh the bridging group vibrations are as already demonstrated but solid state and solution ion pair effects upset the simple theory.

Terminal groups have a very wide range of arrangements, too many to be listed here. For those interested, they have been summarised in reference 147.

Other methods of investigation of organometallic compounds have been used to great effect, including n.m.r., Raman, e.p.r. and Mossbauer spectroscopy, X Ray and neutron diffraction, as well as standard techniques of microanalysis, melting point determinations and other various routine techniques. All have their part to play in the elucidation of bonding, structure and reactions of the ever expanding field of metal carbonyl chemistry.

CHAPTER 2

FORMATION OF TETRACARBONYL COBALTATE (-1)

CHAPTER 2 - FORMATION OF TETRACARBONYL COBALTATE (-1)

1. INTRODUCTION

As already stated, tetracarbonyl cobaltate (-1), $[Co(CO)_4]^-$, is one of the active cobalt carbonyl catalysts, although literature often refers to dicobalt octacarbonyl as the catalyst.

To produce esters from primary and secondary halides, the chemist requires the halide, carbon monoxide, an alcohol and $[Co(CO)_4]^-$ in the presence of a hindered amine[107]. The first stage of the reaction, involving a S_N2 type attack of the anion on the halide to give the alkyl species, is followed by carbon monoxide insertion to give the acyl metal compound. Alcoholysis then removes the acyl group from the metal to give the ester and $HCo(CO)_4$. At this juncture the hindered amine plays its part by converting the hydride to $[Co(CO)_4]^-$, thus eliminating side reactions of $HCo(CO)_4$. The scheme is summarised below[148].

$$RI + [Co(CO)_4]^- \longrightarrow RCo(CO)_4 + I^-$$

$$RCo(CO)_4 + CO \longrightarrow RCOCo(CO)_4$$

$$RCOCo(CO)_4 + R'OH \longrightarrow RCOOR' + HCo(CO)_4$$

$$HCo(CO)_4 + R''_3N \longrightarrow [R''_3NH]^+ [Co(CO)_4]^-$$

Figure 2.1

For the synthesis of symmetric ketones, $Co_2(CO)_8$ reacts with the solvent T.H.F., disproportionating to the anion, as the initial step. Reaction with diaryl - or dialkylmercury compounds and carbon monoxide follows as illustrated[149].

The CO insertion step is, of course, a 1:2 shift of the organic group to give $RCOCo(CO)_3$ which undergoes an oxidative addition reaction with a $RCo(CO)_4$ moiety to give a ketone (by reductive elimination) and $Co_2(CO)_7$.

$Co_2(CO)_8 + THF \rightleftharpoons \{[(THF)Co(CO)_4]^+ [Co(CO)_4]^-\}$

$R_2Hg + \{[(THF)Co(CO)_4]^+ [Co(CO)_4]^-\} \longrightarrow [RCo(CO)_4] + [RHgCo(CO)_4] + THF$

$2[RHgCo(CO)_4] \longrightarrow R_2Hg + Hg[Co(CO)_4]_2$

$Hg[Co(CO)_4]_2 \xrightarrow{h\nu} Hg + Co_2(CO)_8$

$2[RCo(CO)_4] \longrightarrow RCOR + [Co_2(CO)_7]$ *

$[Co_2(CO)_7] + CO \longrightarrow Co_2(CO)_8$

Figure 2.2

* This step was already noted in the literature[150].

$[Co(CO)_4]^-$ has been around the organometallic scene for some time. Hieber et al. produced the anion in the form of a salt of the cobaltous ion[60]. This method initially involved the preparation of $Hg[Co(CO)_4]_2$ which when reacted with $CoCl_2(H_2O)_6$ and NH_4COOMe in concentrated ammonia gave orange-red crystals of $[Co(NH_3)_6][Co(CO)_4]_2$. An alternative preparation was to pass ammonia over '$Co(CO)_4$' (presumably $Co_2(CO)_8$) at 40°C to obtain the mixed metal salt $[Ni(H_2O)_6][Co(CO)_4]_2$ on addition of nickel chloride. The ionic salts were found to be very soluble in water but decomposed readily.

In 1952, in the first in a series of papers on metal carbonyls, Sternberg et al. reviewed earlier substitution reactions of $Co_2(CO)_8$ commenting that these were dissociative reactions and not substitution reactions as previously stated[151].

$[Co(CO)_4]_2 + MeOH \longrightarrow Co_2(CO)_5\ MeOH + 3CO$ (2.1a)

$[Co(CO)_4]_2 + 1.5\ EtOH \longrightarrow Co_2(CO)_5\ 1.5\ EtOH + 3CO$ (2.2a)

$[Co(CO)_4]_2 + 4C_5H_5N \longrightarrow Co_2(CO)_5\ (C_5H_5N)_4 + 3CO$ (2.3a)

$[Co(CO)_4]_2 + 2\ \underline{o}phen \longrightarrow Co_2(CO)_6\ (\underline{o}phen)_2 + 2CO$ (2.4a)

now became

$[Co(CO)_4]_2 + 12\ MeOH \longrightarrow 2[Co(MeOH)_6][Co(CO)_4]_2 + 8CO$ (2.1b)

$[Co(CO)_4]_2 + 12\ EtOH \longrightarrow 2[Co(EtOH)_6][Co(CO)_4]_2 + 8CO$ (2.2b)

$[Co(CO)_4]_2 + 12\ C_5H_5N \longrightarrow 2[Co(C_5H_5N)_6][Co(CO)_4]_2 + 8CO$ (2.3b)

$[Co(CO)_4]_2 + 6\ \underline{o}phen \longrightarrow 2[Co(\underline{o}phen)_3][Co(CO)_4]_2 + 8CO$ (2.4b)

i.e. the general equation was

$$3\,[Co(CO)_4]_2 + xB \longrightarrow 2\,[Co(B)_x]^{2+}\,[Co(CO)_4]_2^- + 8CO \qquad (2.5)$$

with B a Lewis base and x usually 6, sometimes 3 (ophen = ophenanthroline).

The original equations were probably as inaccurate because during the isolation of the product some of the alcohol was lost.

Tertiary butyl alcohol, unlike these above, converts $Co_2(CO)_8$ to $Co_4(CO)_{12}$, this reaction mode being favoured for steric reasons.

The authors went on to put forward a formal mechanism for disproportionation:

$$3B + 3\,[Co(CO)_4]_2 \rightleftharpoons 3\,[BCo(CO)_4]^+\,[Co(CO)_4]^-$$

$$2\,[BCo(CO)_4]^+ \longrightarrow 2B + 2Co^{2+} + 8CO + 2e^-$$

$$[BCo(CO)_4]^+ + 1e^- \longrightarrow B + {}^{\bullet}Co(CO)_4$$

$${}^{\bullet}Co(CO)_4 + 1e^- \longrightarrow [Co(CO)_4]^-$$

Overall:

$$3\,[Co(CO)_4]_2 \rightleftharpoons 2Co[Co(CO)_4]_2 + 8CO$$

Figure 2.3

If two radicals recombined, $Co_2(CO)_8$ would result which would re-enter the cycle. The driving force for the disproportionation is the formation of the symmetric $[Co(CO)_4]^-$ which possesses the rare gas structure. Although the cation has the same rare gas structure it is less symmetrical and hence it was argued, less favoured.

Electron transfer has been used to obtain $Co(CO)_4^-$ using sodium amalgam as the reducing agent.

$$2Na + [Co(CO)_4]_2 \longrightarrow 2Na^+\,[Co(CO)_4]^- \qquad (2.6)$$

This has its drawbacks, being potentially more hazardous (e.g. when preparing the amalgam) and there being a chance that $Hg\,[Co(CO)_4]_2$ could be made instead.

The strong base induced disproportionation gave higher yields of anion (based on the amount of $Co_2(CO)_8$ present) with some of the carbon

monoxide being converted to the carbonate ion (e.g. 2.7a).

$$Co_2(CO)_8 + CO + 4OH^- \longrightarrow 2\,[Co(CO)_4]^- + CO_3^{2-} + 2H_2O \qquad (2.7a)$$

This can be contrasted with Hieber's description of the reaction:

$$\underset{\text{(dimer)}}{3Co(CO)_4} + 2OH^- \longrightarrow 2HCo(CO)_4 + \underset{\text{(polymer)}}{Co(CO)_3} + CO_3^{2-} \qquad (2.7b)$$

Reaction between $Co_2(CO)_8$ and dimethyl amine also leads to reaction of carbon monoxide with the amine.

$$3\,[Co(CO)_4]_2 + 24Me_2NH \longrightarrow 2\,[Co(Me_2NH)_6]\,[Co(CO)_4] + 8HCONMe_2 + \underset{\text{4MeNH complexed}}{} \qquad (2.8)$$

The extra moles of dimethyl amine are complexed by the anion via hydrogen bonding, as shown by infrared spectroscopy.

At the time of the original work, Emeleus and Anderson took the view that there were two reactions, equation 2.9 a & b, and with weak bases only the second equation held[40].

$$3Co_2(CO)_8 + 4OH^- \longrightarrow 4Co(CO)_4H + 2CO_3^{2-} + 2Co(CO)_3 \text{ polymer} \qquad (2.9a)$$

$$3Co_2(CO)_8 + 4H_2O \longrightarrow 4Co(CO)_4H + Co(OH)_2 + 4CO \qquad (2.9b)$$

Infrared spectroscopy being in its infancy at this time, other techniques were utilised to determine the concentrations of carbonyl species. One such method was based on the principle of a gasometric technique[152] and was successful in calculating amounts of $Co_2(CO)_8$, $[Co(CO)_4]^-$, and $HCo(CO)_4$ present in a reaction mixture. All three species can be quantitatively decomposed in excess iodine, evolving characteristic amounts of carbon monoxide according to the equations.

$$Co_2(CO)_8 + 2I_2 \longrightarrow 2CoI_2 + 8CO \qquad (2.10)$$

$$2[Co(CO)_4]^- + 3I_2 \longrightarrow 2CoI_2 + 8CO + 2I^- \qquad (2.11)$$

$$2HCo(CO)_4 + 3I_2 \longrightarrow 2CoI_2 + 8CO + 2HI \qquad (2.12)$$

$[Ni(\underline{o}phen)_3]^{2+}$ will only react with the anion and the product can be separated from $Co_2(CO)_8$ (being insoluble in water and hydrocarbon solvents unlike $Co_2(CO)_8$). This can in turn be decomposed quantitatively

by iodine and the carbon monoxide liberated used as a measure of the original anion concentration. The amount of $Co_2(CO)_8$ is then obtained by subtraction from the original total carbon monoxide evolution. The success of the method was due to its rapidity, accuracy and suitability for small amounts of material.

If further determination of the anion concentration was required, application of gravimetric techniques to the solid $[Ni(\underline{o}phen)_3]^{2+}$ salt would suffice.

The first concerted study of cobalt carbonyl structures by infrared spectroscopy followed a few years later[85]. Under the microscope, metaphorically speaking, were $HCo(CO)_4$, $Co_2(CO)_8$, $[Co(CO)_4]^-$ and $Co_4(CO)_{12}$. The authors, taking due account of the Pauling concept of the double bond character of the metal - carbon bond, wrote the M - C bond as M ----- C ===== O to indicate fractional bond order due to the resonance between M ——— C ——— $\ddot{O}$: and M ←——— C ═══ O:, i.e. they pictured such a bond as intermediate between a ketenic type carbonyl (bond order 2) and a carbon monoxide type carbonyl (bond order 3).

Two preparative routes to the anion were used[153,151]

a) $HCo(CO)_4 + C_5H_5N \longrightarrow [C_5H_5NH]^+ [Co(CO)_4]^-$ (2.13)

b) $3\,[Co(CO)_4]_2 + 12py \longrightarrow 2\,[Co(py)_6]^{2+}\,[Co(CO)_4]_2^- + 8CO$ (2.14)

where py = pyridine.

The tetrahedral structure assigned to $[Co(CO)_4]^-$ resembled $Ni(CO)_4$ in that it contained four carbonyl groups, although the molecule is charged. The bonding was considered to be sp^3 hybrid (Fig. 2.4).

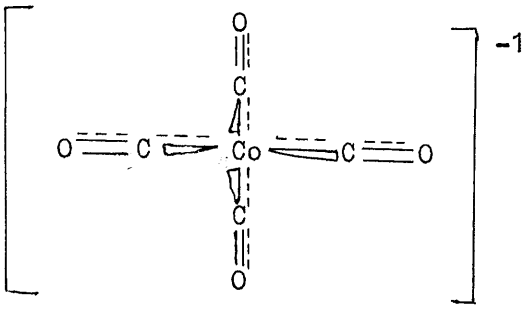


Figure 2.4

The i.r. spectrum showed one band in the carbonyl region at 1883 cm^{-1} (cf $Ni(CO)_4$ - 1 band at 2060 cm^{-1}) plus another band at 553 cm^{-1} (assigned to Co - C - O bend). The low value of the carbonyl frequency was accounted for by the charge on the molecule which, on the basis of Pauling's principle of electron neutrality of the central atom, would affect the bond order of the M - C≡O bond system. For $Ni(CO)_4$ the average M - C bond order is 1.67 and the average carbon - oxygen bond order is 2.33. The corresponding values for $[Co(CO)_4]^-$, after adjusting to dissipate the -1 charge on cobalt, are 1.87 and 2.13 respectively. This lower carbonyl bond order is reflected by the lower absorption frequency.

Apart from e.g. base induced disproportionation[154], and halide induced disproportionation which will be dealt with later, research has established other routes to the anion. One popular method was to reductively cleave the $Co_2(CO)_8$ dimer by sodium amalgam[155]. The effectiveness of this preparation in different solvents was investigated e.g. benzene[151], diethyl ether or dimethyl ether[156], hexane[157] and T.H.F.[158]. Closer study of this reaction showed that it was not solely the anion that was produced but compounds of mercury and $Co_2(CO)_8$, e.g. $Hg[Co(CO)_4]_2$, were also present[159], although this was supposed to be an intermediate stage. This contamination was annoying since the most likely method of separation required fractional sublimation and so other methods were sought.

One such route already in the literature was the reduction of $Co_2(CO)_8$ by lithium wire in T.H.F.[160]. Another involved the reaction:

$$[M(L)(CO)_x]_2 + 2KH \longrightarrow 2K[M(L)(CO)_x] + H_2 \qquad (2.15)$$

$$L = CO,\ PPh_3,\ cp.$$

This received close attention since the only other product was hydrogen[161] and quantitative yields were achieved in under twelve hours over the temperature range -78^oC to $+ 30^oC$ (the reaction taking 12 hours at -78^oC or 1 hour at 0^oC followed by half an hour at 25^oC).

A sodium amalgam treatment of $cpCo(CO)_2$ in T.H.F.[162] yielded $[Co(CO)_4]^-$ together with the interesting binuclear cobalt radical $[cpCo(CO)]_2^-$.

Use of sodium - potassium alloy in T.H.F. was reported as being a quick efficient preparation of metal carbonyl anions[163] (reaction times at room temperature being less than one and a half hours). For $Co_2(CO)_8$ a 96% yield was achieved with potassium being the predominant cation. $KCo(CO)_4$ could also be prepared using C_8K[164] i.e.

$$Co_2(CO)_8 + 2C_8K \xrightarrow[THF]{25^oC} 2KCo(CO)_4 + \text{graphite} \qquad (2.16)$$

The benefit of the route was impossibility of the hydrido species being formed.

By now more elegant preparations were being cited. One involved cleavage of the dimer by trialkylborohydride (e.g. $LiEt_3BH$, $Li(\text{sec } C_4H_9)_3BH$ and $K(\text{sec } C_4H_9)_3BH$) which was hailed as a convenient one flask preparation of metal alkyls, metal acyls and mixed metal compounds[165]. It also used cheap starting materials (i.e. the metal dimer), effected rapid, near quantitative synthesis of the required anions and only needed simple apparatus (one Schenk flask), the only expense being the alkyl borohydride.

$$L_n(CO)_xM - M(CO)_xL_n + 2M'R_3BH \longrightarrow 2M'[L_n(CO)_xM] + 2R_3B + H_2 \qquad (2.17)$$

$$M' = Li \text{ or } K$$

For $Co_2(CO)_8$ in T.H.F. using $LiEt_3BH$ the reaction is almost instantaneous

giving $LiCo(CO)_4$ with no detectable metal carbonyl biproduct.

The production of $TlCo(CO)_4$ in 1974 showed enterprise in the choice of synthetic methods[166]. Four methods were employed

a) Metathesis of $NaCo(CO)_4$ with thallium (I) salts in water.

b) Metal exchange between $Hg[Co(CO)_4]_2$ and thallium metal.

c) Reaction of thallium metal with $Co_2(CO)_8$

d) Reduction of $Tl[Co(CO)_4]_3$ by thallium metal.

The authors gave a detailed study of i.r. spectra of the compounds formed in different solvents.

Recently more exotic reactions have been employed in obtaining $[Co(CO)_4]^-$. Reduction of $Co_2(CO)_8$ by a sodium dispersion[167] or by NaH/tAmONa in T.H.F. (tAm = tertiary - amyl) (eqn. 2.18)[168] have given the desired product.

$$NaH/tAmONa + Co_2(CO)_8 \xrightarrow[THF]{CO} NaCo(CO)_4 \qquad (2.18)$$

The latter route requires two hours at 25°C and two hours at 63°C for 98% conversion. The higher temperature is to rid the solution of an unknown cobalt carbonyl species which absorbs at 1955 and 1940 cm^{-1}. Basically this reaction is a mixture of disproportionation and reduction of $Co_2(CO)_8$; the tAmONa part causing disproportionation according to the usual stoichiometry and the sodium hydride causing reduction.

Combining ammonia with $HCo(CO)_4$ to give $[NH_4]^+[Co(CO)_4]^-$ is well documented[169]. Recently a structure determination of related compounds, i.e. $[NR_3H]^+[Co(CO)_4]^-$, by X Ray diffraction has given the first direct evidence of the interaction between a coordinating proton and a carbonyl metallate anion[170], this being relevent to the hydrogen transfer from metal hydrides to organic substrates[171].

The compounds were prepared by the direct combination of the amine and the metal carbonyl components under argon and in hexane at -78°C. The adducts $NR_3HCo(CO)_4$ were formed within the time of mixing and isolated

as colourless, air and moisture sensitive, solids which were slightly soluble in hydrocarbons. The molecular structure of the compound with R = Et consisted of discrete pair units formed by $[NEt_4H]^+$ and $[Co(CO)_4]^-$ ions with hydrogen associated with the nitrogen located on the three-fold axis of symmetry of the pair, coincident with the three-fold crystallographic axis. A similar structure was derived for the compound with R = Me, except the $[Co(CO)_4]^-$ moiety slightly deviated from C_{3v} symmetry and there was a shorter N.....Co contact distance, as a result of the smaller steric hindrance of the methyl group.

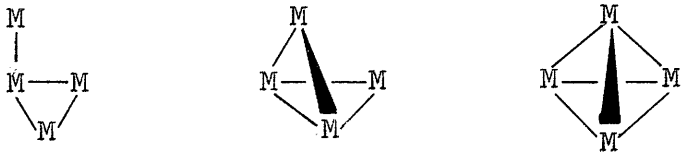
Evidence of interaction within the $[NR_3H]^+ \ldots\ [Co(CO)_4]^-$ unit persisting in hydrocarbon solvents (i.e. forming contact ion pairs) is furnished by its i.r. spectrum (consistent with C_{3v} symmetry of the anion which gives rise to three carbonyl absorptions), freezing point depressions (the methyl adduct in benzene showing no dissociation in solution), and n.m.r. studies (showing the protonic nature of the nitrogen bonded hydrogen).

In other compounds $[Co(CO)_4]^-$ is shown to be almost a regular tetrahedron e.g. in the complex[172], $[(Ph_3P - C_5H_4)Co(CO)_2]^+ [Co(CO)_4]^-$, which is formed by reacting $Co_2(CO)_8$ with triphenyl phosphiniocyclopentadieneide in T.H.F.

Other information concerning the $Co(CO)_4$ moiety is obtainable from its electronic absorption spectrum[173] and Extended Huckel Theory calculations[131]. Electronic absorption spectra of $M(CO)_4$ type molecules showed that closed shell compounds (M = Ni, Pd, Pt) exhibited $d \rightarrow \pi^*$ carbonyl bands in the U.V. region whereas in open shell compounds (M = Co, Rh, Ir) relatively low energy $\sigma \longrightarrow t_2(d)$ transitions are observed, with $d \rightarrow \pi^*$ type transitions at higher energy. These open shell molecules proved to have low lying ligand to metal charge transfer transitions (c.f. the knowledge that metal carbonyl complexes have low lying excited states of metal $\longrightarrow$ ligand charge transfer type). $Co(CO)_4$ itself is a seventeen valence

electron species and shows a marked C_{3v} distortion from a regular tetrahedron, as expected, evidence being provided by e.p.r. and i.r. spectra. The experiments were conducted in a matrix of carbon monoxide[131a]. Reactions of the anion have been utilised in many areas of both inorganic and organic chemistry. Substitution of $Co_2(CO)_8$ by PR_3 to give species of the type $[Co(CO)_3L_2]\,[Co(CO)_4] + CO(L = PR_3)$ have been shown to involve $^{\bullet}Co(CO)_4$ radicals[129] by studies using stopped - flow and O_2 scavenger techniques.

$[Co(CO)_4]^-$ has been used with closed metal carbonyl trimers to synthesise tetranuclear mixed metal clusters[174]. This method has successfully produced $HCoRu_3(CO)_{13}$, $HCoRu_2Os(CO)_{13}$, $HCoRuOs_2(CO)_{13}$, $HCoOs_3(CO)_{13}$ and $[CoRu_3(CO)_{13}]^-$. The suggested mechanism involves an initial attack by the nucleophilic $[Co(CO)_4]^-$ on the electropositive carbon of a bound carbon monoxide group. Elimination of this molecule with concomitant metal - metal bond formation would yield structure (a) (Fig. 2.5). This would be followed by closure, via a nucleophilic attack at the other metal atoms, with carbon monoxide elimination to give structure (c) via (b).



(a) (b) (c)

Figure 2.5

This is a simplified approach to a very complex mechanism which the authors did not claim to understand fully.

$[Co(CO)_4]^-$, under a variety of guises, will react with organic halides to give ketonic derivatives. The reaction of $Co_2(CO)_8$ to form the anion) with benzyl halide will give exclusively benzophenone whereas the benzoyl halide under the same circumstances leads to a cobalt carbonyl cluster[175] i.e.

$$PhCOCl + Co_2(CO)_8 \longrightarrow PhCCo_3(CO)_9 \qquad (2.19)$$

When an acid and a methanolic solution of $[Co(CO)_4]^-$ are in the company of an organic halide, the halide is replaced by the hydrogen or the formyl group. This is often accompanied by aldehyde formation. Hydrogenolysis is often the only reaction, the formylation reaction only becoming significant with aliphatic and benzyl halides[176].

$$3R_3C\text{-}X + 2\,[Co(CO)_4]^- + 3H^+ \longrightarrow 3R_3C\text{-}H + 2Co^{2+} + 3X^- + 8CO \qquad (2.20)$$

Under neutral conditions the reaction is very slow, but acidic conditions make for a rapid reaction.

The reaction scheme for the acidic reactions is shown in Fig. 2.6[176].

$$Co_2(CO)_8 \xrightarrow{MeOH} [Co(MeOH)_6]^{2+}\,[Co(CO)_4]^-_2$$

$$[Co(CO)_4]^- + H^+ \rightleftharpoons HCo(CO)_4$$

$$R\text{-}X \xrightarrow{[Co(CO)_4]^-} R\text{-}Co(CO)_4 \xrightarrow[(a)]{HCo(CO)_4} R\text{-}H + Co_2(CO)_8$$

$$R\text{-}Co(CO)_4 \xrightarrow[(b)]{CO} RCCo(CO)_4 \xrightarrow{HCo(CO)_4} R\text{-}CHO + Co_2(CO)_8$$

(RCCo(CO)$_4$: C=O)

Figure 2.6

The ratio of hydrogenated : formylated products depends on the relative rates of (a) and (b). Electron withdrawing substituents of R were found to favour (a).

Reactions between organic halides and $[Co(CO)_4]^-$ have been used to prepare carboxylic acids[113,177-8], esters[107], lactones[105,179-80], amides[107] and ketones[181-2].

Imidoyl halides have been shown to react by way of nucleophilic displacement of the halide producing complexes containing η^1 - imino - acyl ligands $[Co(CO)_4]^-$ being a weak nucleophile will induce head to tail coupling of two imidoyl groups by the incorporation of two anions, the bis-imidoyl ligand chelating one cobalt atom while one of the carbon

atoms bridges the two mutually bonded cobalt atoms (established by X Ray crystallographic analysis)[183].

Stoichiometric hydrogenation using $[Co(CO)_4]^-$ was brought up to date in 1980 with an article describing the reaction of methanolic solutions of $[Co(CO)_4]^-$, in the presence of an acid, with olefins[184].

$$3\ >C=C<\ +\ 2\,[Co(CO)_4]^-\ +\ 6H^+ \longrightarrow 3\ >CH-CH<\ +\ 2Co^{2+}\ +\ 8CO \qquad (2.22)$$

This is a more effective usage of cobalt carbonyl derivatives giving a three-fold increase in yield.

(c.f. $>C=C<\ +\ 2CoH(CO)_4 \longrightarrow H>C-C<H\ +\ Co_2(CO)_8$ in hydrocarbon solvents).

In the polar solvents, e.g. methanol (MeOH), $HCo(CO)_4$ dissociates to H^+ and $[Co(CO)_4]^-$ so the easier to handle anion can be used in the presence of acid to achieve similar results with higher yields. The reaction also gives highly selective hydrogenation e.g. the regioselective reduction of 6-methylene tetracycline derivatives to give preferentially the α-epimer in similar yields as obtained by using $RhCl(Ph_3P)_3$ as the catalyst.

Reactions with chlorosilanes in ethereal solvents led to recognition of different pathways[185], the route taken depending on the acidity of chlorosilane and the basicity of the solvent. For group IV derivatives of the metal carbonyls the normal course of reaction is self elimination[186,154].

$$R_3EX + ML_n^- \longrightarrow R_3EML_n + X^- \qquad (2.23)$$

where E = C, Ge, Sn, Pb ; ML_n^- = $[Co(CO)_4]^-$, $[Mn(CO)_5]^-$, $[Fe(CO)_2cp]^-$ etc. ; R = alkyl, aryl or halogen, cp = η^5-C_5H_5.

This route is not widely applicable to silicon derivatives.

For $[Co(CO)_4]^-$ experiments there were two potential sites of attack on the anion - at the metal centre and at a carbonyl ligand.

Stronger Lewis acids e.g. $MeSiCl_3$ and $SiCl_4$ attack the carbonylic oxygen to give, via an adduct, the clusters $R_3SiOCCo_3(CO)_9$. Weak acids

e.g. Me_3SiCl, attack at cobalt giving $Me_3Si\text{-}Co(CO)_4$. Me_2SiCl_2, being intermediate, gives a complex reaction, suggesting borderline behaviour. This is in contrast to the heavier group IV elements, e.g. germanium derivatives, which tend to form metal - metal bonds[187], e.g.

$$[Co(CO)_4]^- + ClGeH_2GeH_2Cl \longrightarrow Co(CO)_4GeH_2GeH_2Co(CO)_4 \qquad (2.24)$$

(this reaction completes the sequence Ge-M, Ge-Ge-M, M-Ge-Ge-M and $Ge_2(Ge)M$). All species are susceptible to hydrogen substitution and Ge-M bond cleavage.

This can be compared with the behaviour of Group III derivatives of $[Co(CO)_4]^-$ which favours metal - metal bond formation. Hieber and Teller initiated investigation in this field, obtaining $In[Co(CO)_4]_3$, $Tl[Co(CO)_4]_3$, and $TlCo(CO)_4$ by direct reaction of the two finely divided metals under vigorous conditions (200°C, 200 atm. carbon monoxide)[142]. More recently $Br_2GaCo(CO)_4$.T.H.F. has been prepared by reacting $GaBr_3$ and $NaCo(CO)_4$ in T.H.F.[188]. Further reaction with Thallium (I) acetylacetonate (Tl acac) will surrender $Br(acac)GaCo(CO)_4$. The monohalo species $XGa[Co(CO)_4]_2$. THF (X = Cl, Br) and acac - $Ga[Co(CO)_4]_2$ were prepared initially from $GaCl_3$ and $NaCo(CO)_4$ with the latter two by substitution of the chloro compound. Reaction of the anion with $InBr_3$ (1:3 ratio) gave $In[Co(CO)_4]_3$ with similar derivatives realised using $TlCl_3$. A 1:2 ratio of anion to $InBr_3$ gave the T.H.F. adduct $BrIn[Co(CO)_4]_2$.THF. This is not a good Lewis base and so easily loses the T.H.F. when the bromide is replaced by a third $[Co(CO)_4]^-$ molecule.

Further work on the thallium derivatives led to interesting comments on the bonding and structure in such compounds. As mentioned earlier, four routes to $TlCo(CO)_4$ were used[166]. The i.r. spectrum of the salt was studied in non polar solvents and had three principal absorption bands in the carbonyl stretching region ($2A_1 + E$) consistent with the

structures (I) and (II) (Fig. 2.7) of C_{3v} symmetry with (I) dominating in such solvents.

$Tl - Co(CO)_4$ (I) $Tl - OC - Co(CO)_3$ (II)

Figure 2.7

With all three bands at higher frequency than $[Co(CO)_4]^-$ itself, this was regarded as an indication of the transfer of charge from cobalt to thallium, by means of a metal - metal covalent bond. In water the anion acts as "free" tetrahedral $[Co(CO)_4]^-$, as in acetonitrile (MeCN) and MeOH. The $Tl[Co(CO)_4]_3$ compound could be obtained by the action of $Co_2(CO)_8$ on $TlCo(CO)_4$ in T.H.F.[188], the equilibrium lying far to the right.

Edgell and his co-workers studied the crystal structure of $TlCo(CO)_4$ w.r.t. its chemistry and possible solution state[189]. The crystal contained discrete Tl^+ and $[Co(CO)_4]^-$ ions arranged in a sodium chloride type structure with the closest approach of the metals being approximately 0.35 Å longer than the sum of their covalent radii. However in solvents of low dielectric constant evidence pointed to some degree of Tl - Co covalent bonding and tight ion pairs. High dielectric solvents (e.g. H_2O, dimethyl sulphoxide DMSO, and dimethyl formamide (D.M.F.), favoured existence of the compound as free ions or solvent separated ion pairs. The reaction of $TlCo(CO)_4$ with triphenyl phosphine varies with solvent. In D.M.S.O., even at elevated temperatures, no reaction was observed but in dichloromethane $Tl[Co(CO)_3PPh_3]_3.2CH_2Cl_2$ could be isolated and is found to be identical to the product of the reaction between $Tl[Co(CO)_4]_3$ and triphenyl phosphine in dichloromethane.

$NaCo(CO)_4$ will react with $In[Co(CO)_4]_3$ in T.H.F. and dichloromethane giving $In[Co(CO)_4]_4^-$ but the corresponding Tl salt disdains to undergo

such reaction. It will however, as earlier predicted in the literature[188], insert into $Co_2(CO)_8$ with dichloromethane as the solvent to give $Tl[Co(CO)_4]_3$ at room temperature. $TlCo(CO)_4$ also exhibits Lewis acid properties, reacting with $[Ph_3(PhCH_2)P][Co(CO)_4]$ to give $[Ph_3(PhCH_2)P][Tl\{Co(CO)_4\}_2]$ which has a complicated i.r. spectrum dominated by $TlCo(CO)_4$ bands and the $[Co(CO)_4]^-$ (as a loose ion pair) band. Absorptions assigned to $Tl[Co(CO)_4]_2^-$ itself were 2020m, 1937m and 1904s cm^{-1} with this anionic species being present, in dichloromethane solutions of $[(PhCH_2)Ph_3P][Tl\{Co(CO)_4\}_2]$, in comparable amounts with $TlCo(CO)_4$.

Addition of either $TlCo(CO)_4$ or $[(PhCH_2)Ph_3P][Co(CO)_4]$ shifted the equilibrium to the left;

$$Tl[Co(CO)_4]_2^- \rightleftharpoons TlCo(CO)_4 + [Co(CO)_4]^- \qquad (2.25)$$

Later Schramin and Zink reported on the metal - metal charge transfer in $TlCo(CO)_4$[190]. The energy of this band varied according to the solvent whereas for $PPNCo(CO)_4$ [PPN = μ-nitrido-bis(triphenyl phosphorus)] the band is independent of solvent. The charge transfer band was unusual because the system was not strongly covalent bound (such as in metal dimers and bridged metal dimer complexes). The i.r. showed one or three absorptions depending on the solvent whereas that of $PPNCo(CO)_4$ only had one unique absorption. Charge transfers were found to be associated with solvents in which $TlCo(CO)_4$ exhibited three i.r. bands, indicative of ion pairing (i.e. acetonitrile, phenylnitrile, 2-propanol dichloromethane, toluene and benzene) and is influenced by both the dielectric constant and the basicity of the solvent.

Reduction of $[Co(CO)_4]^-$ with sodium in liquid ammonia provided the interesting species $[Co(CO)_3]^{3-}$ when a 1:3 ratio of starting materials was used, the reaction taking eight hours at -78^oC to proceed[191]. The i.r. showed two broad carbonyl stretches at very low energy (1744m,

and 1600vs cm^{-1} in an oil mull). Naphthalene - sodium in T.H.F. will produce a similar compound[192] but is very slow (40-48 hours later at -80°C, the i.r. will still show substantial amounts of unreacted $NaCo(CO)_4$) although it has the advantage of proceeding in an environment free of strong base. The reaction of these complexes with various group IV halides gave new five coordinate species (isolated as $[Et_4N]^+$ salts) e.g.

$$[Co(CO)_3]^{3-} + Ph_3ECl \longrightarrow [(Ph_3E)_2Co(CO)_3]^- \qquad (2.26)$$

where E = Sn, Ge or Pb, and the ratio of Ph_3ECl : $[Co(CO)_3]^{3-}_4$ is at least 2:1. The i.r. of such derivatives suggests D_{3h} symmetry. Compounding $Co(CO)_4X$, (X^- = halide ion) with magnesium amalgam in the presence of a Lewis base (B) produces species of the type $B_xMg[Co(CO)_4]_2$ (x = 4 for $[Co(CO)_4]^-$ complexes of Mg^{2+} but will be two for more nucleophilic anions e.g. $[Fe(CO)_2cp]^-$)[193]. The compounds are useful as metallating reagents. They are not strongly dissociated in T.H.F.[194] and are strongly attacked by oxygen to give magnesium oxide plus the corresponding transition metal carbonyl dimer. With alkylhalides and phenols, alkyl and hydrido transition metal complexes are obtained. Reactions with other metals have been looked into in detail. Metallic lead or tin will react with $Co_2(CO)_8$ to give $M[Co(CO)_4]_4$ with the lead derivative capable of further reaction with sodium or lithium to give the corresponding $[Co(CO)_4]^-$compound[195]. Polar solvents e.g. ether or acetone, will coordinate to the lead containing compounds but tin seems unable to extend its coordination number to accommodate the solvent.

With platinum, derivatives of the type $M\text{-}PtL_2\text{-}M$ (M^-= $[Co(CO)_4]^-$ and other anionic species) have been characterised[196] and are linear in structure.

Recently the first heteronuclear gold - cobalt cluster $Au_6(PPh_3)_4[Co(CO)_4]_2$ (Fig. 2.8) was prepared using $LiCo(CO)_4$ and $[Au_8L_7][NO_3]_2$ ($L = PPh_3$) in a 2:1 ratio in T.H.F.[197]. After half an hour a red brown solid could be isolated with its X Ray determined structure as below:

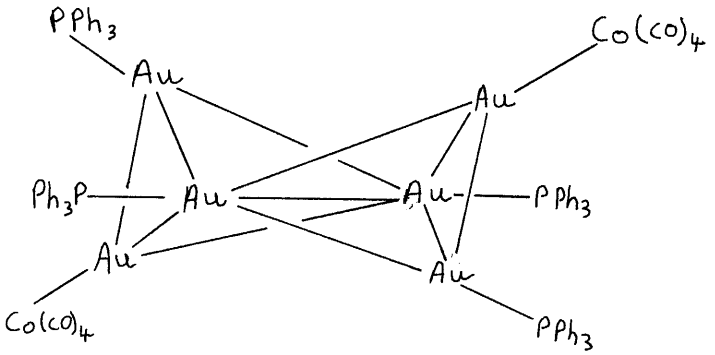


Figure 2.8

Group III derivatives have not been neglected. A new class of compound was synthesised of the type $M[(X_3B)_nMe(CO)_p]$ where M = alkali metal, quarternary ammonium or phosphonium cation, X = H or F, Me = transition metal Mn, Tc, Re, Co, Rh or Ir, n = 1 or 2 (but only two when X = H and the atomic number of Me is greater than 28), p = 4 (for group VIII Me) or 5 (for group VII B Me)[198]. The compounds can alternatively be written as a salt, $M^+[(X_3B)_nMe(CO)_p]^-$ and have potential scope as drying agents, or when X = F as catalysts in polymerisation reactions, or when X = H as selective reducing agents.

Tetraphenyl phosphonium and arsonium ions react with the less nucleophilic carbonyl anions to yield stable crystalline products[199]; with more nucleophilic anions e.g. $[cpFe(CO)_2]^-$, the products are $PhFe(CO)_2cp$ and substantial amounts of the dimer $[cpFe(CO)_2]_2$.

$[Ph_4As]^+$ does not react with $[Co(CO)_4]^-$ at room temperature in T.H.F. but addition of diethyl ether provides the crystalline salt $[Ph_4As]^+ [Co(CO)_4]^-$. The i.r. of the salts in T.H.F. is very simple compared with the alkali metal derivatives (which have ionpairing effects). Because of the synthetic uses, the reaction between $Co_2(CO)_8$ and benzyl halides has come in for a lot of attention. $NaCo(CO)_4$ is well known for it catalytic carbonylation of organic halides[113,177], with its methanolic solution and organic halides leading to stoichiometric hydrohalogenation and formylation[176]. Benzyl bromide or iodobenzene will react to give an ester and symmetric ketone (after decomposition of the reaction mixture by iodine - methanol)[175]. A kinetic study of the oxidative addition of benzyl chlorides to $[Co(CO)_4]^-$ has been made with the rate of reaction being determined in a range of solvents. This showed the importance of assistance for the leaving group by the cation and the protic solvents.

Alkyl cobalt carbonyl species being highly reactive, their formation can only be inferred by the disappearence of the $[Co(CO)_4]^-$ from the i.r. spectrum. The reaction is first order in each of the reactants[200]

i.e. $$\text{rate} = k_2 [PhCH_2Cl][NaCo(CO)_4] \qquad (2.27)$$

A study of activation parameters and kinetic data concluded the following:

a) Alcohols are amongst the best solvents.

b) In aprotic solvents the rate decreases in the sequence anisole > isopropyl ether > n propyl ether > T.H.F. > MeCN > D.M.F.

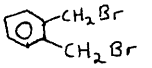
c) Crown ethers lower the reaction rate by a factor of 420 in D.M.F., 30 in anisole, 6 in 2-methyl -2 butanol and 1.3 in MeOH.

d) Rate varies with cation in T.H.F. in the sequence $Na^+ > K^+ > Cs^+ > Li^+ > [Et_3N]^+ - CH_2C_6H_5$.

e) Substituents on the benzene ring of $PhCH_2Cl$ have little effect on rate but electron releasing groups enhance the rate.

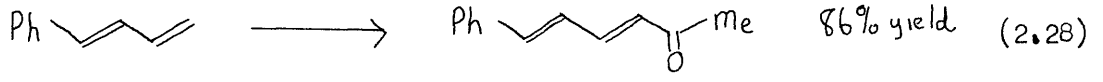
f) Reaction is strongly influenced by a large entropy term.

Again ion pairing has a large effect on the reaction.

$[Co(CO)_4]^-$ can react with compounds of the type 

X = Br or Cl in benzene or T.H.F. at slightly elevated temperatures to give indanones, with napthalene type derivatives giving the corresponding substituted indanones[182].

Phase transfer reagents are becoming more popular. Quarternary ammonium halides which can form relatively stable free radicals can be carbonylated to carboxylic acids by reaction with carbon monoxide, cobalt carbonyls, methyl iodide, sodium hydroxide and benzene[201] e.g. in the reaction shown in 2.28, carbonylation of the ammonium salt is the unwanted side reaction, destroying the phase transfer catalyst.



(2.28)

The intermediate stage is formation of an acetylcobalt tetracarbonyl complex. The reaction time is measured in days but proves that phase transfer reagents such as quarternary ammonium halides will be carbonylated and so should be avoided in slow transfer processes.

Synthesis of acyl cobalt carbonyl compounds by means of RCH_2X and $[Co(CO)_4]^-$ was investigated using phase transfer and three phase catalysis [111], showing the inefficiency of the latter method. For the two phase system, $n\text{-}Bu_4NCl$ was the catalyst with the water insoluble $n\text{-}Bu_4NCo(CO)_4$ ion pair found in the organic layer and $NaCo(CO)_4$ in the aqueous layer. This enabled continuous migration of the ammonium cation between the two phases:

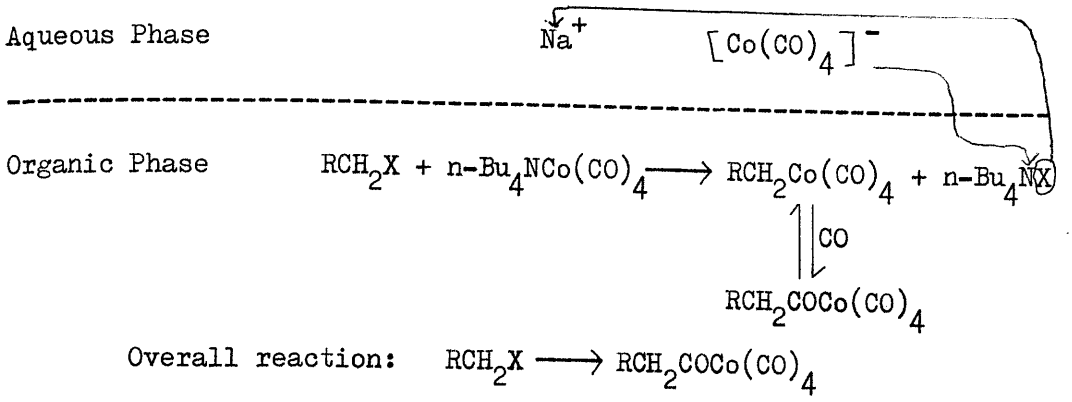


Figure 2.9

For the three phase system, catalysis is by anionic exchange:

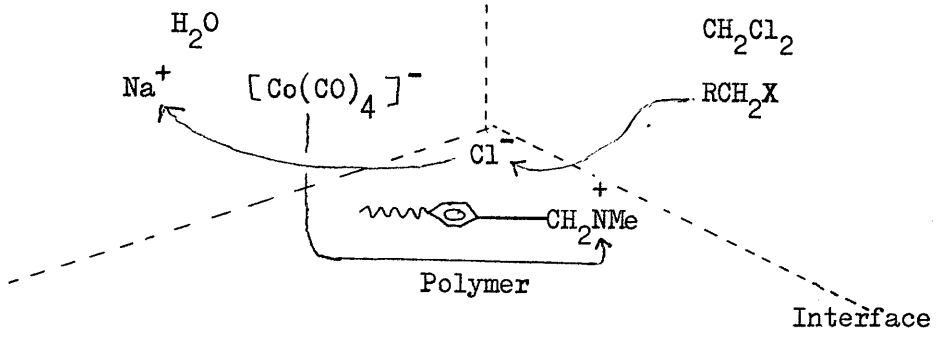
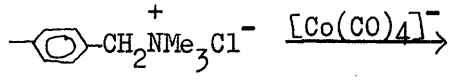
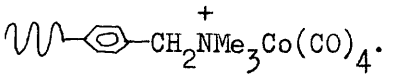


Figure 2.10

The quarternary ammonium group is now fixed to a crosslinked polystyrene matrix to set up the exchange   . The quarternary ammonium catalyst is necessary to speed up the rate of reaction.

$RCH_2COCo(CO)_4$ could not be isolated but undergoes further reaction with triphenyl phosphine giving $RCH_2COCo(CO)_3PPh_3$[106].

The two phase system also revealed that the observed rate constants (rate = $k_{obs}[PhCH_2Br]$) varied linearly with the amount of the ammonium salt present and for a given concentration of $n\text{-}Bu_4NCl$, the value of k_{obs} depended on the solvent[202a]. This implied that the two phase system worked without the ammonium cation travelling back and forward between the phases, the concentration of $[Co(CO)_4]^-$ being regulated

in the organic layer by a simple anion exchange through the interface according to Fig. 2.11 and the reactive species is the ion pair $[n\text{-}Bu_4N]^+[Co(CO)_4]^-$.

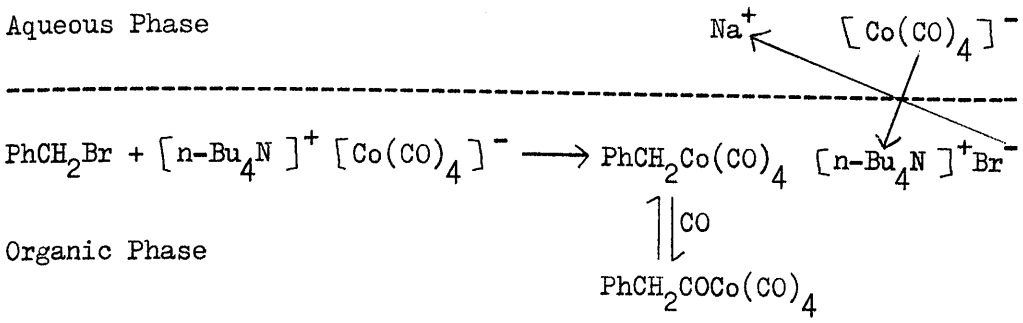


Figure 2.11

The same group also showed that in carbonylation of $PhCH_2Br$ using a two phase system (aqueous and organic phases) the catalytic species $n\text{-}Bu_4NCo(CO)_4$ remained in the organic layer while the product $[PhCH_2CO_2]^-$ remained in the aqueous layer, thus effective separation of the product and catalyst had been achieved[202b].

Bringing this aspect of anionic behaviour up to date, a recent paper described the reduction of metal carbonyl halides and metal carbonyls by quarternary ammonium borohydrides in phase transfer catalysed reactions[203]. In this instance the borohydride is generated in the aqueous phase and transferred to the organic phase (CH_2Cl_2) as the quarternary salt, this large cation then being able to stabilise the newly formed metal carbonyl anion. This method can be used to convert $Co_2(CO)_8$ to $[Et_4N]^+[Co(CO)_4]^-$ in half an hour using Et_4NX (X = Cl,Br) as the transfer agent. The attraction for this preparation of $[Co(CO)_4]^-$ is the freedom from mercury contamination or highly reactive alkali metal cations, although the authors acknowledged that the sodium - potassium reduction method is the best for $[Co(CO)_4]^-$ formation in terms of time and yield. The topic of phase transfer catalysis has been recently reviewed in depth[204].

As most of the research to be discussed in this, and succeeding, chapters concerns the $[Co(CO)_4]^-$ anion in various solvents and with different cations, the effect of such external influences on the i.r. spectrum of the anion is of great importance. Much has been published on this theme, with the forerunners in the field being W. Edgell and his co-workers and to a lesser extent M.Y. Darensbourg and D.J. Darensbourg .

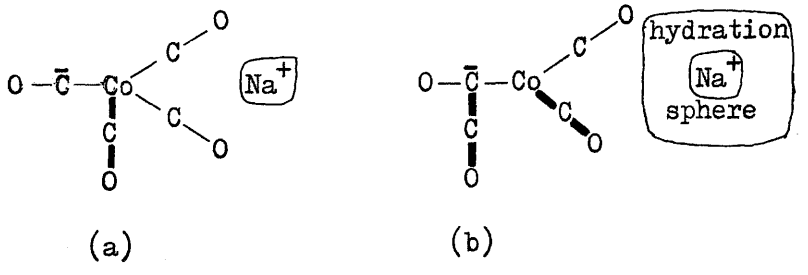
The solvent plays an important role in the assistance of the leaving group in the displacement of halides from benzyl chloride by $[Co(CO)_4]^-$ as already noted[200]. The spectrum of $[Co(CO)_4]^-$ with a large, bulky organic cation, e.g. $[Ph_4P]^+$, has been shown to be much more simple than for $Na^+[Co(CO)_4]^-$ [199].

Edgell began his own scrutiny of the $NaCo(CO)_4$/solvent system in the mid-sixties. The first of many papers drew attention to the very solvent dependent carbonyl stretching frequencies of $NaCo(CO)_4$ [205]. The number of i.r. absorptions ranged from three in pure T.H.F. (one main band + two side bands) to one in water and D.M.F. Higher concentrated solutions in T.H.F. only exhibited two absorptions, i.e. the third band only appeared on dilution. Less than 10% of water was required to remove the two side bands, leaving the symmetrical main peak. D.M.F. had the same effect when it constituted 50% of the solvent. The actual wavenumber of the main band shifted with solvent e.g. in T.H.F. the value is 1886 cm^{-1} , but is 1892 cm^{-1} in D.M.F. and 1919 cm^{-1} in water. These marked differences are much more pronounced than in the neutral metal carbonyls. From the i.r. spectrum and conductance experiments (which demonstrated distinct association of the two ions in T.H.F.), Edgell proposed the presence of different types of ion sites. Group theory predicts two carbonyl stretches for a Td point group, A_1 and F_2 with only the latter being i.r. active. If the symmetry of the

molecule is lowered, the degeneracy of F_2 is partially or completely lifted and A_1 becomes i.r. active. This effect can also be produced by an external field deforming the tetrahedral symmetry of the ion. Thus the splitting of F_2 and the intensity of A_1 serve as a measure of the dissymmetry of the ion.

In T.H.F. the effective symmetry must be less than tetrahedral and so Edgell assigned 1886 and 1889 (shoulder)cm^{-1} to the F_2 mode with 1858 cm^{-1} assigned to an A_1 mode (which arises from the splitting of the F_2 mode in Td to A_1 + E modes in C_{3v}); the A_1 symmetric mode of Td is the highest stretching frequency observed in compounds, and above 2000 cm^{-1} for metal carbonyls[89]. For $[Co(CO)_4]^-$, the actual value for the A_1 mode is 2005 cm^{-1} (see later - ref. 209a). For water and D.M.F. the anion retains its tetrahedral symmetry and so only one band is seen.

Conductance measurements in T.H.F. showed triple and quadruple ions present in substantial amounts in concentrated solutions yet ion pairs dominated at low concentrations. Because the number of absorptions increased with dilution, the ion pairs must have an effective symmetry of less than Td, unlike the ion pairs in T.H.F./water or pure water. Dissymmetry was therefore a result of the anisotropic complexing of the ions with a T.H.F. molecule and with the close proximetry of the sodium cation in the ion pair, as shown in Fig. 2.12.



(a) (b)

Figure 2.12.

In the presence of water, the sodium ion gathers a hydration sphere around it, making the ionic radius much larger and so increasing the

distance between the two parts of the ion pair. This in turn nullifies the distortion effect of the non hydrated Na^+ ion on the electronic symmetry of the anion and so the effective symmetry of the anion is again raised to tetrahedral.

The changes in carbonyl stretching frequencies with solvent was rationalised in terms of solvent/solute interactions and not in terms of two separate species. This type of interaction has been shown to be important for solutes of neutral molecules[206].

The increase in size of solvent induced shifts of $[Co(CO)_4]^-$ w.r.t. neutral metal carbonyls e.g. $Ni(CO)_4$ and $Fe(CO)_5$ was taken as characteristic of the charge on the anion and was a consequence of increased participation of antibonding π orbitals of carbonyl in the bonding of these groups to the metal in the anionic species[207].

Following this line of investigation led to elaboration of the above theory. The effect of $A^+[Co(CO)_4]^-$, (A = K, Li, Na) in a variety of solvent systems was explored[208]. In D.M.F. and D.M.S.O., $NaCo(CO)_4$ gives rise to one absorption but with T.H.F., D.M.E. and pyridine a complex spectrum results. Water was placed in a separate category because of broad Hbond type absorptions. Li^+ and K^+ salts in T.H.F. were similar to the Na^+ case. From the results four different types of anions were postulated.

a) Solvent Separated Ion Pairs

$[Co(CO)_4]^-$ in a solvent surrounded environment (the only peak in a single absorption spectrum or the dominant peak of a complex spectrum); the anion is allowed to interact, by vibration, with the solvent whilst isolated from the effects of the cation (hence the difference in i.r. values of the "free anion" in T.H.F. (1880 cm^{-1}) and water (1915 cm^{-1}). The anion will remain approximately Td.

b) Unsymmetrical Solvent Interaction with Anion

In solvents such as T.H.F., the anion is in an unsymmetrical environment. This can be caused by the cation perturbing $[Co(CO)_4]^-$ or by the solvent strongly solvating the anion such that the anion vibrational degeneracy is lifted.

c) Triple Ions and d) Higher Clusters

Both c) and d) have been previously described.

The i.r. spectrum of $LiCo(CO)_4$ in T.H.F. indicated that Li^+ is more strongly solvated by T.H.F. than either Na^+ or K^+, hence the majority of the anions are in a solvent surrounded system, (in the latter situation there is a mixture of symmetric and unsymmetric environments of the anion). Further delving into the i.r. spectrum of $NaCo(CO)_4$ in T.H.F. led to the band around 1880 cm^{-1} being divided into three components. Low temperature work was carried out and the various frequencies assigned[209].

Environment	i.r. (cm^{-1})	Ramam (cm^{-1})	Assignment
I	1886	1889 (0.76)[a]	Td, F_2
		2005 (~0.1)	Td, A_1
II	1855	1857 (0.74)	C_{3v} A_1
	1899	1905 (0.76)	C_{3v} E
	2003	2005 (~0.1)	C_{3v} A_1

[a] Single depolarisation measurement made at band maximum, 1890 cm^{-1}.

Table 2.1

i.e. there are two ion types in T.H.F. solutions of $NaCo(CO)_4$. C_{3v} symmetry occurs because of the profound effects of Na^+ in the central ion pair, lowering the symmetry of the anion (via a monodentate or tridentate interaction - for bidentate interactions C_{2v} symmetry would be expected).

Type I environment leads to the anion being in a free ion site or a solvent separated ion pair site, and type II environment gives a monodentate or tridentate contact ion pair site or a free ion site with a significant unsymmetrical solvation. Type II could also be caused by anions in a triple ion site with small anion - anion coupling. This can be contrasted with work using D.M.S.O. as the solvent. Here the cation frequency is independent of the salt anion and the dominant structures are loose ion pairs and "free" ions[210].

The various absorptions had already been connected with the different modes of vibration[211].

Normal Mode	Symm.	Description[a]	D.M.F. Raman(cm^{-1})	D.M.F. ir(cm^{-1})	H_2O Raman(cm^{-1})	H_2O ir(cm^{-1})
$\tilde{\nu}_1$	A_1	$\tilde{\nu}$ C-O	2002		2019	
$\tilde{\nu}_2$	A_1	$\tilde{\nu}$ Co-(CO)	431		432	
$\tilde{\nu}_3$	E	δ Co-C-O				
$\tilde{\nu}_4$	E	δ(OC)-Co-(CO)	91		88	
$\tilde{\nu}_5$	F_2	$\tilde{\nu}$ C-O	1890	1888	1912	1914
$\tilde{\nu}_6$	F_2	$\tilde{\nu}$ Co-(CO)	556	555	558	
$\tilde{\nu}_7$	F_2	δ Co-C-O	523	527	522	
$\tilde{\nu}_8$	F_2	δ(OC)-Co-(CO)				
$2\tilde{\nu}_9$	F_1^2	δ Co-C-O	710		714	

[a] $\tilde{\nu}$ stretch, δ angle deformation; these approximate descriptions refer to atom displacements.

Table 2.2

Again the frequency shift of C - O stretching frequencies $\tilde{\nu}_1$ and $\tilde{\nu}_5$ from D.M.F. to water suggested that the anion is solvated in water and probably in D.M.F. (water is recognised as the better solvating agent). Further pursuit along this track showed that the $NaCo(CO)_4$ molecule apparently has only one i.r. absorption band in D.M.S.O. nitromethane

D.M.F., pyridine, hexamethylphosphoric triamide (H.M.P.A.) and MeCN[212], but on closer inspection (and by use of band analysis)two bands were found. The main component is assigned to the F_2 mode of vibration with the weak side band due to the A_1/F_2 mode of the $Co(CO)_3$ (^{13}CO) band with the weak side band due to the A_1/F_2 mode of the $Co(CO)_3$ (^{13}CO) this isotopic band), the main $[Co(^{\prime 2}CO)_4]^-$ anion still enjoying Td symmetry. Such solvents with high donor ability will result in $NaCo(CO)_4$ being solvent separated since the small positively charged sodium ion will prefer attachment to the electronegative centre of the solvent rather than the weakly negative charge of the anion (because of dispersion of charge over the large molecule).

Inspection of $NaCo(CO)_4$ with oxetane, D.M.E. and T.H.F. over a wide temperature range and with the aid of computer analysis enlarged the number of different ion sites to three[213]. These were:

Type I - solvent separated ion pair site of Td structural symmetry.

Type II - contact ion pair site of C_{3v} structural symmetry.

Type III - triple ion site of C_{3v} symmetry in the solution structure at the $[Co(CO)_4]^-$ ion.

Oxetane, with one band (apart from possible isotopic side bands) only has type I ions. D.M.E. has an i.r. spectrum with three bands, two of them (at 1854 and 1899 cm^{-1}) disappearing as the temperature drops and the strongest one (at 1887 cm^{-1}) increasing in intensity. This implies the presence of type I and II ions. T.H.F. now has five i.r. bands in the spectrum at 300 K. Only the signal at 1885 cm^{-1} increases with falling temperature, the others being grouped according to their rate of disappearence. All three ion types are present for $[Co(CO)_4]^-$ in T.H.F. and these are tabulated in Table 2.3.

Site Type	$\bar{\nu}$ cm^{-1}	Relative Intensity	Symmetry	Assignment
I	1887	s	Td	F_2
II	1889	s	C_{3v}/Td	E/F_2
	1856	m		A_1/F_2
III	1906	s	C_{3v}'/Td'	E/F_2
	1846	m		A_1/F_2

Table 2.3

For type I to be a regular tetrahedral structure (and thereby give only one i.r. absorption) the carbonyl groups of the anion and the sodium cation must have solvent molecules as their nearest neighbours. T.H.F. and D.M.E. have low dielectric constants and so most of type I site ions should be associated as solvent separated ion pairs as illustrated in Fig. 2.13a. This is equivalent to a solvent surrounded free ion. For type II ions, the near neighbours of $[Co(CO)_4]^-$ make one carbonyl group non equivalent with the others and in so doing lifts the degeneracy of the F_2 mode. This can occur when an anion replaces a solvent molecule in the proximetry of Na^+ and forms the contact ion pair shown in Fig. 2.13b. Local symmetry should become C_{3v} but the anion exhibits C_{3v} distortion from Td symmetry due to the effective field geometry (C_{3v}). For the triple ion two i.r. active modes are again expected (C_{3v}' and Td' dual symmetry where there is no coupling between the anions), as described in Fig. 2.13c.

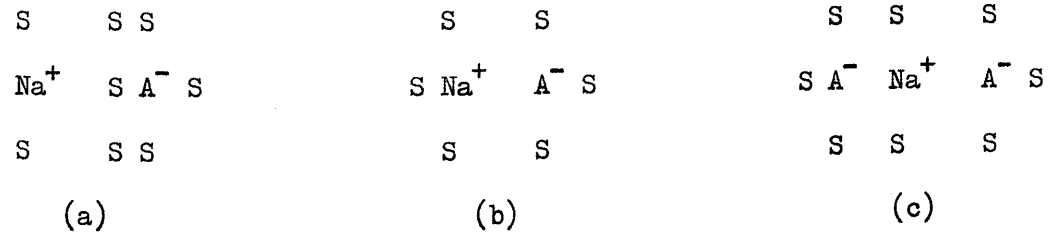


Figure 2.13

where S = solvent molecule and $A^- = [Co(CO)_4]^-$.

The area under each absorption band is approximate to the proportion of anion tied up in that structure. From this it was calculated that in T.H.F., the anions consist of 40% type I, 50% type II and 10% type III i.e. the T.H.F. molecule is almost as effective as the $[Co(CO)_4]^-$ anion in obtaining a near neighbourhood position to Na^+ in the competing process:

$$S_x Na^+ SA^- \rightleftharpoons S_x Na^+ A^- S \qquad (2.29)$$

Oxetane is a more strained ring molecule with a greater donor ability and so a greater percentage of type I sites should be present, as indeed experimental evidence bears out (with 100% type I). D.M.E. is a poorer electron donor but compensates for this by interacting with Na^+ in a bidentate manner (see Fig. 2.14) to the extent of two or three molecules interacting with one cation. This has the effect of increasing the stability of type I sites w.r.t. the other sites and so this is the most popular ion site in D.M.F.

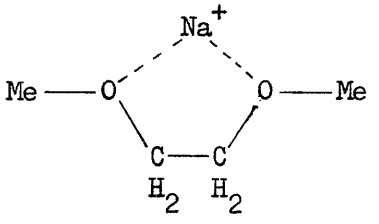


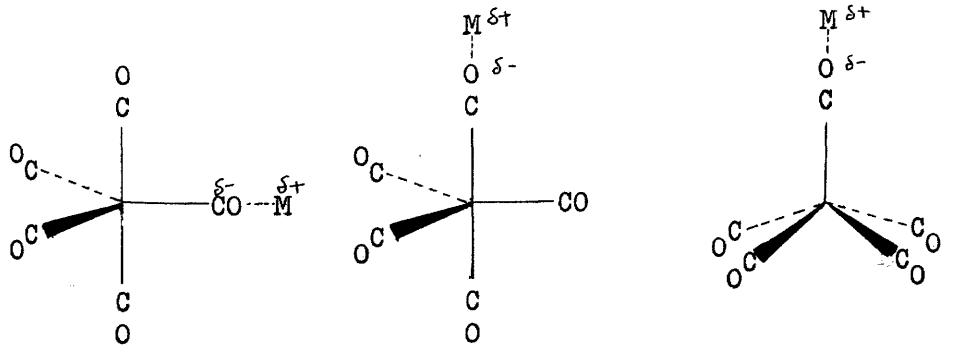
Figure 2.14

Finally in this field, studies with crptend C221 (with T.H.F., D.M.E., tetrahydropyran (T.H.P.) and 2-methyl tetrahydrofuran (2-M.T.H.F.) as the solvents) showed conversion of the mixture of ion sites normally found in each system to a single ion site[214]. For T.H.F. and D.M.E. this was ion type I of Td symmetry, whilst in T.H.P. and 2-M.T.H.F. the ion sites show C_{2v} symmetry i.e. the perturbation influence of Na^+ has not been totally removed.

Similar work was being done at the same time on manganese - carbonyl - ligand systems. Ion pair species of C_{3v}, with the alkali metal ion bound to the carbonyl oxygen, was found for $LiMn(CO)_5$ and $NaMn(CO)_5$ in

ether solvents[215]. In T.H.F. the Na^+ salt exhibited an equilibrium between solvent separated and contact ion pairs. Addition of Mg^{2+} gave a compound containing Mg - OC interactions.

Diethyl ether is a weaker coordinating and less polar solvent than T.H.F. and as a consequence gives rise to more complicated i.r. spectra. The unpeturbed $[Mn(CO)_5]^-$ has D_{3h} symmetry and the solutions in diglyme and T.H.F. bear witness to this. In ether both the Na^+ and Li^+ salts have an i.r. spectrum which varies with concentration and the alkali counterion and has three carbonyl absorptions. Addition of a crown ether (dicyclohexyl - 18 - crown - 6) to complex Na^+ gives almost free anion in ether with the i.r. showing a molecule of D_{3h} symmetry (1871 (E') and 1902 cm^{-1} (A') c.f. T.H.F. values of 1863 and 1898 cm^{-1}). The three possible ions in this system were ion pair, multi associated ion pair and free $[Mn(CO)_5]^-$. Ion pairing was visualised as occurring through the carbonyl oxygen - alkali metal interaction for the three bands in diethyl ether, being verified by the variation of the i.r. spectrum with cation. Because of the low value of the lowest absorption a bridging carbonyl species must be involved i.e. cation - anion - interaction is not at the metal centre. Of the three possible structures considered (C_{2v}, C_{3v} and C_{4v} symmetry) the second was the most likely in view of the i.r. and force constant information.



(a) $C_{2v}(5)$ (b) $C_{3v}(4)$ (c) $C_{4v}(3)$

Figure 2.15 ( ) = ir stretching modes.

Later Darensbourg, Darensbourg and their team took up the cause and examined the alkali metal ion interactions with manganese carbonylate derivatives[216]. Infrared indicated the contact ion interactions observed for a series of $NaMn(CO)_4L$ (L = CO or phosphine substituents) in T.H.F. was the cation interacting with the oxygen of an equitorial carbonyl group. Conductimetric titrations showed involvement of two to four H.M.P.A. molecules per Na^+ or Li^+ and one 15 - crown - 5 - macrocyclic polyether per Na^+ or Li^+ in the formation of solvent separated ion pairs and free ions. From the information gleaned from these and kinetic experiments, equilibria were established as shown.

$Mn(CO)_4L^-.....\overset{+}{S}MS.....Mn(CO)_4L^-$ $\qquad$ $L(OC)_3MnCO....M^+....OCMn(CO)_3L^-$

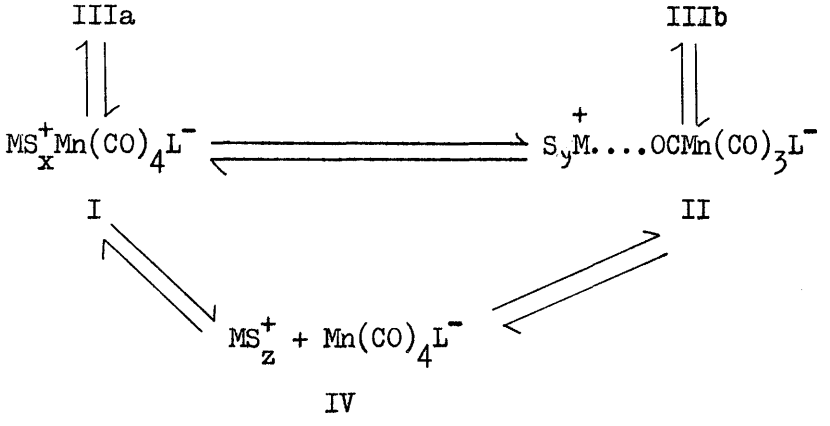


Figure 2.16

For $LiMn(CO)_5$, $[Na^+.15 - crown - 5 -][Mn(CO)_5]$ and $[Na^+ \propto HMPA][Mn(CO)_5]$ in T.H.F. I, IIIa and IV predominate while a mixture of all five will be present in $NaMn(CO)_5$ and $NaMn(CO)_4L$ (at concentrations of around 0.01 molar). $Li^+(THF)_n$ is a more stable solvate than $Na^+(THF)_n$ and so lends itself to a symmetric environment for $LiMn(CO)_5$. The cation will interact with the most electron rich carbonyl oxygen, which will belong to the equatorial carbonyl (as proven by the linear $\bar{\nu}$ (CO) stretching constant). The resultant interaction then enhances the complexed carbonyl group's π acceptor ability (stronger π bonding ligands have already been shown to prefer the equatorial position of a trigonal bipyramid[217]).

The spectrum of $NaMn(CO)_5$ in T.H.F. was re-examined and the stretching modes previously noted in reference 215 reassigned.

2009w cm^{-1} - A_1(C_{2v} local symmetry); 1902 cm^{-1}-degenerate (accidental) $A_1 + B_1$; 1875 cm^{-1} - B_2; 1829 cm^{-1} - carbonyl complexed to Na^+, A_1.

The relationship between solvent and metal carbonyls was researched with a view to correlating the type of solvent to its effect on the i.r. absorption frequencies of the carbonyls[218]. Solvent polarity alone cannot account for such magnitudes of shift and certain non polar solvents, e.g. carbon tetrachloride, produce larger shifts than some polar solvents, e.g. water. A simple donor - acceptor approach was favoured with the oxygen atom of the carbonyl group behaving as a donor towards the solvent. This would imply a relationship between its properties and the solvent acceptor number to exist where the solvent acceptor number is a measure of the electrophilic properties of the solvent[219]. Edgell's work[208,209a,212] did not satisfactorily account for the C - O stretching vibrations of the anion in six different solvents giving a single absorption band, $\bar{\nu}_m$. This band, with computer aid, showed an extremely weak band on the low frequency side assigned to the ^{13}C species[212] which followed the same trend as $\bar{\nu}_m$ (as a function of solvent). A correlation between solvent acceptor number and $\bar{\nu}_m$ does exist, with increase in the acceptor number causing a slight increase in wavenumber corresponding to the shortening of the C - O bond. Cobalt in the oxidation state -1 leads to a stronger Co - C π bond and longer C - O bonds. Electrophilic solvent attack at the oxygen atoms of carbonyl groups leads within the $[Co(CO)_4]^-$ anion to a fall of electron density in particular around the cobalt atom which induces a weakening of the Co - C π bonds and shortening of the C - O bonds. This will be a small effect, as is the extent of charge transfer between the complex unit and the solvent.

The motion of the alkali metal in solutions of $A^+[Co(CO)_4]^-$ has aroused interest. Infrared frequencies due to such interactions are usually in the 200 cm^{-1} region of the spectrum. Pure $A^+[Co(CO)_4]^-$ solution and $A^+[Mn(CO)_5]^-$ in T.H.F. (A = Li, K, Na) were prepared. Infrared absorptions at 407, 190 and 150 cm^{-1} were observed for Li^+, Na^+ and K^+ - cobalt salts respectively with the manganese compounds 20 - 30 cm^{-1} higher in frequency[220]. These absorptions are caused by vibration of the cation within the ion pair. The work was extended to include D.M.S.O., pyridine and piperidine as solvents and in all instances the band associated with the alkali ion vibration was observed[221]. The actual frequency of vibration depends on the anion in T.H.F. (e.g. $[Co(CO)_4]^-$, I^-, $[BPh_4]^-$) but is independent of the anion in D.M.S.O. Change of solvent induces a change in frequency. From these observations it was deduced that structure existed at the alkali ion in solution and had a sufficiently long lifetime to form a cage in which the cation could vibrate. The cages were either composed of solvent molecules surrounding the cation or had an anion in close association with the cation in addition to the solvent molecules, both cages capable of co-existing in solution. In D.M.S.O. the first cage structure will dominate (and so virbations are made independent of the anion) while the second cage is the important one in T.H.F. to give anion dependent absorptions[209b]. $NaCo(CO)_4$ can be contrasted with the behaviour of $TlCo(CO)_4$ in solution. For the latter in T.H.F. there is a tight ion pair site predominating with small amounts of solvent separated ion pair and of $\{Tl[Co(CO)_4]_2\}^-$ present, whereas for the Na^+ compound there are similar ion sites but the tight ion pair involves association through an oxygen atom and very little covalent character[189]. This results in the two similar compounds undergoing different types of reaction e.g. $In[Co(CO)_4]_3$ plus the sodium salt will form $In[Co(CO)_4]_4^-$ smoothly but $Tl[Co(CO)_4]$ will not react.

Similar results were obtained using dichloromethane as the solvent. This arises because of the greater stability due to Tl - Co covalent interaction preventing further reaction.

Thermodynamic studies of the ionic solutions (in different solvents) have been used to discuss the relevence of ion - solvent molecule interactions in the gas phase to ionic solutions and has been comprehensively reviewed[222].

Finally ionic interactions of this nature are not confined to solvent situations. Interaction between highly acidic countercations and carbonyl groups of mononuclear carbonylmetallates in the solid state have been recorded[223]. Recently the solid compound $LiCo_3(CO)_{10}$ - iPr_2O has been prepared and studied by i.r. spectroscopy and X Ray crystallography[224]. The structure consists of Li^+ and $[Co_3(CO)_{10}]^-$ ions with the cation roughly tetrahedrally surrounded by one ether oxygen and three carbonyl oxygens of three different cluster units. The i.r. spectra (mull and diethyl ether solution) were consistent with small amounts of clusters with edge bridging carbonyl groups in solvent dependent equilibria with clusters containing terminal groups only. Addition of T.H.F. to a diethyl ether solution of the complex lowered the acidity of Li^+ (by coordination to the more basic T.H.F.) and promotes a structure containing face bridging carbonyl groups, at the expense of edge bridging groups. Because the acidity of Li^+ is enhanced in the solid state, the structure containing edge bridging carbonyl groups is stabilised. This is a good example of varied structural changes arising from a change in the acid/base properties of the system.

2. HALIDE INDUCED DISPROPORTIONATION OF $Co_2(CO)_8$ IN T.H.F. AND ITS REACTIONS

Halide induced disproportionation of $Co_2(CO)_8$ is an attractive proposition because it eliminates byproducts e.g. mercury - cobalt carbonyl salts are formed when reduction by sodium amalgam is employed[159].

Disproportionation by bases can give problems if the base becomes involved in further reactions with the product or combines with the liberated carbon monoxide to form amides[83]. Halides however give a clean reaction (e.g. K_2CoCl_4), the only other species produced being Co^{2+} (as the halide salt CoX_2). The reaction is smooth and rapid in T.H.F. and by strategic use of crown ethers, can be made to proceed in hydrocarbon solvents[182]. Disproportionation need not be limited to $Co^{o} \longrightarrow Co^{2+} + 2Co^{-1}$; the reaction shown in equation 2.30 has been cited, this being $4Co^{o} \longrightarrow Co^{3+} + 3Co^{-1}$ [40].

$$2Co_2(CO)_8 + 6HSR + 3OH^- \longrightarrow 3Co(CO)_4H + [Co(SR)_6]^{3-} + 4CO + 3H_2O \quad (2.30)$$

Disproportionation of $Co_2(CO)_8$ [and $Co_4(CO)_{12}$] will occur in T.H.F. but the reaction time is measured in days. At higher concentrations (i.e. greater than 10^{-2} molar) $Co_2(CO)_8$ dimerises to $Co_4(CO)_{12}$. This behaviour can be rationalised by comparing the mechanism of Sternberg et al. for formation of the anion[151] with the mechanism of Ungvéry and Markó for $Co_4(CO)_{12}$ formation[152]. The latter have shown that the rate of dimerisation varies as the square of the initial concentration of $Co_2(CO)_8$. For production of $[Co(CO)_4]^-$ the attack of T.H.F. on $Co_2(CO)_8$ is the rate determining step and the valence disproportionation is assumed to be first order in $Co_2(CO)_8$. Thus increasing the concentration of $Co_2(CO)_8$ will enhance formation of $Co_4(CO)_{12}$. Addition of NaX or LiX (X = Br, I) to $Co_2(CO)_8$ in T.H.F. will give $[Co(CO)_4]^-$ as the only carbonyl containing species in solution within five minutes; $n\text{-}Bu_4NX$ takes a little longer, about ten minutes. Earlier work in this department[182,225] showed that the anion formed in this manner would react as expected e.g. with α,α'- dibromo-o-xylene to give 2-indanone.

To separate the effects that a) the cation and b) the halide might be exerting on the reaction and to establish what effect, if any, the

byproduct $CoBr_2$ had, a series of lithium salts and halide salts were tested.

Using a stoichiometry of 3:4 for $Co_2(CO)_8$:lithium bromide, LiBr, disproportionation to the anion in T.H.F. takes less than five minutes at room temperature and under nitrogen while under a carbon monoxide atmosphere five - ten minutes is required (Fig. 2.17a). The extra time for the latter experiment was needed to convert the last 10% of $Co_2(CO)_8$. Halving the amount of LiBr added (in a nitrogen atmosphere) will leave trace quantities of $Co_2(CO)_8$ in solution after twenty four hours (but is still faster than solvent disproportionation alone). If at this intermediate stage of reaction the atmosphere is changed to carbon monoxide a mixture of $Co_2(CO)_8$ and $[Co(CO)_4]^-$ persists - Fig. 2.17d.

The stoichiometric amount of lithium tetrahydroborate, $LiBH_4$, will give complete conversion to anion within fifteen minutes under carbon monoxide according to equation 2.31.

$$Co_2(CO)_8 + 2LiBH_4 \longrightarrow 2\,[Co(CO)_4]^- + H_2 + 2BH_3.T.H.F. \qquad (2.31)$$

Addition of iron tris phenanthroline chloride, $[Fe(\underline{o}phen)_3]Cl_2$, led to isolation of a red solid shown to be $[Fe(\underline{o}phen)_3]^{2+}[Co(CO)_4]_2$ (Fig. 2.18).

The more bulky salt lithium tetrafluoroborate, $LiBF_4$, was next in line. It gave very slow disproportionation to anion with some $Co_2(CO)_8$ and $Co_4(CO)_{12}$ also present in solution, having not gone to completion after 72 hours (under carbon monoxide) implying that any reaction was due to solvent intervention. Possibly the low solubility of $LiBF_4$ in ethers, unlike $LiBH_4$, accounts for the lack of activity.

Similar results were obtained using lithium hexafluorophosphate, $LiPF_6$, under carbon monoxide as shown in Fig. 2.19b; if anything the rate of reaction is slower.

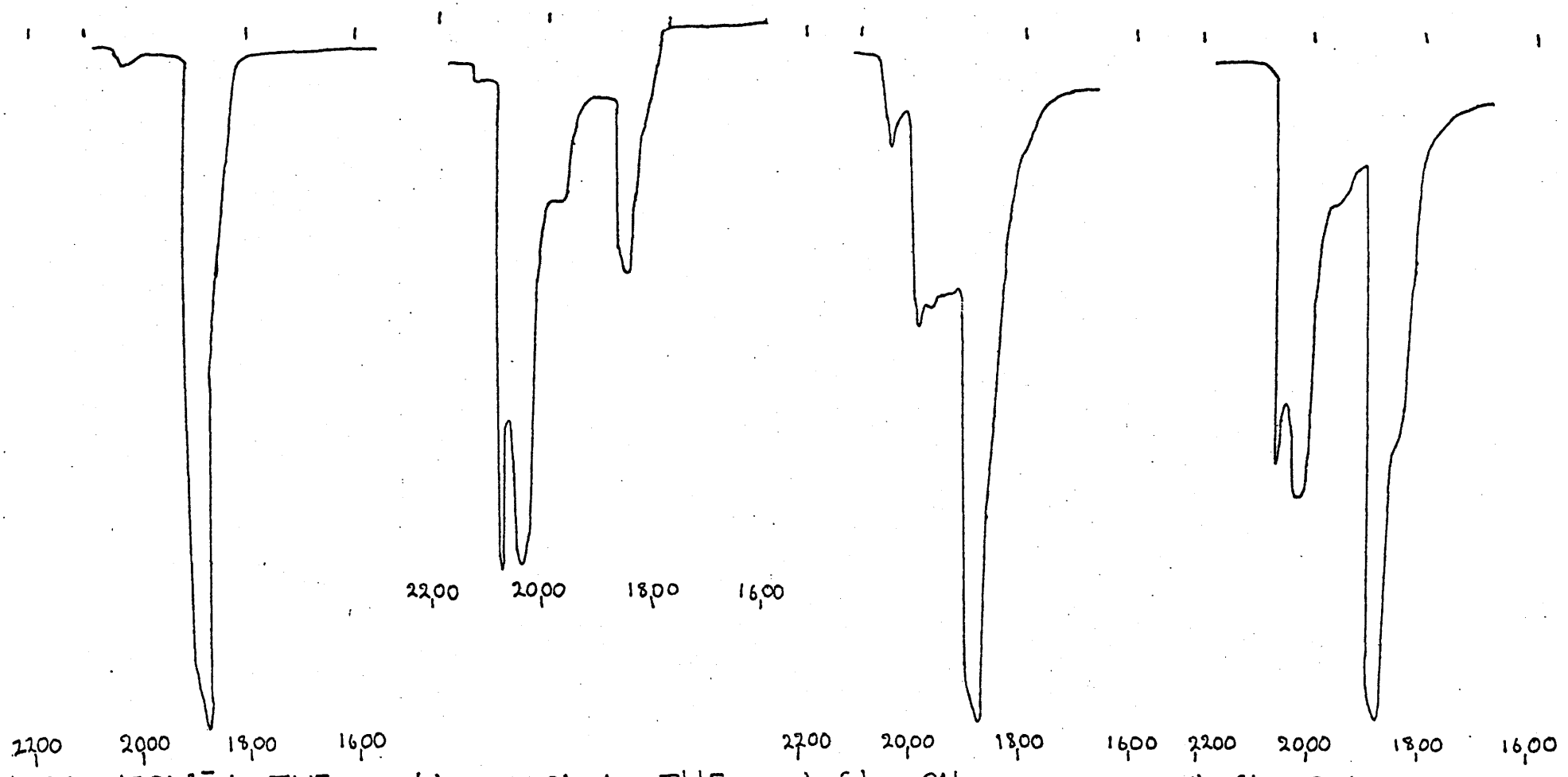

2200 2000 1800 1600
2200 2000 1800 1600
2200 2000 1800 1600
2200 2000 1800 1600
a) $[Co(CO)_4]^-$ in THF
b) $Co_2(CO)_8$ in THF
c) after 21hrs
d) after 25hrs

Figure 2.17

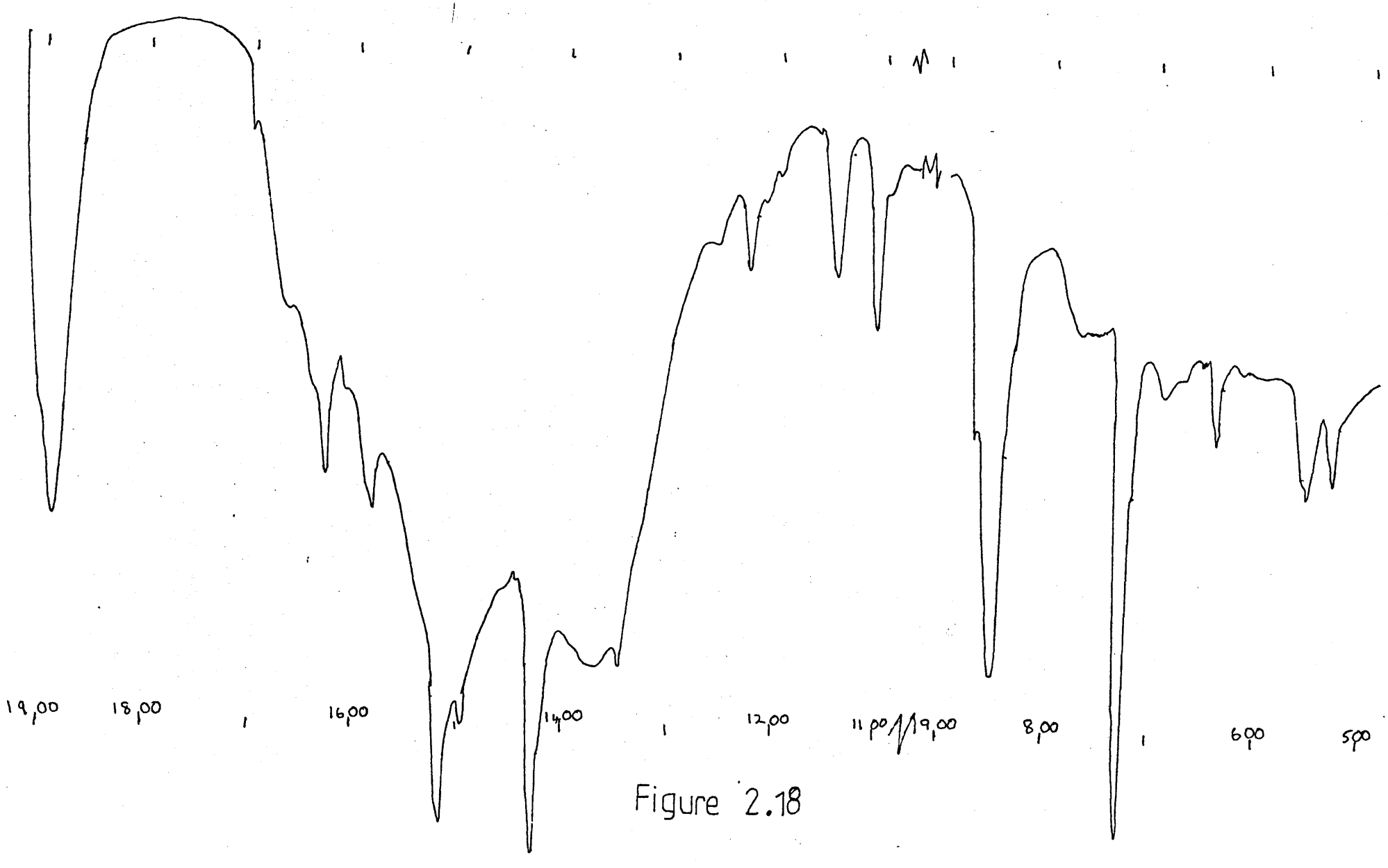
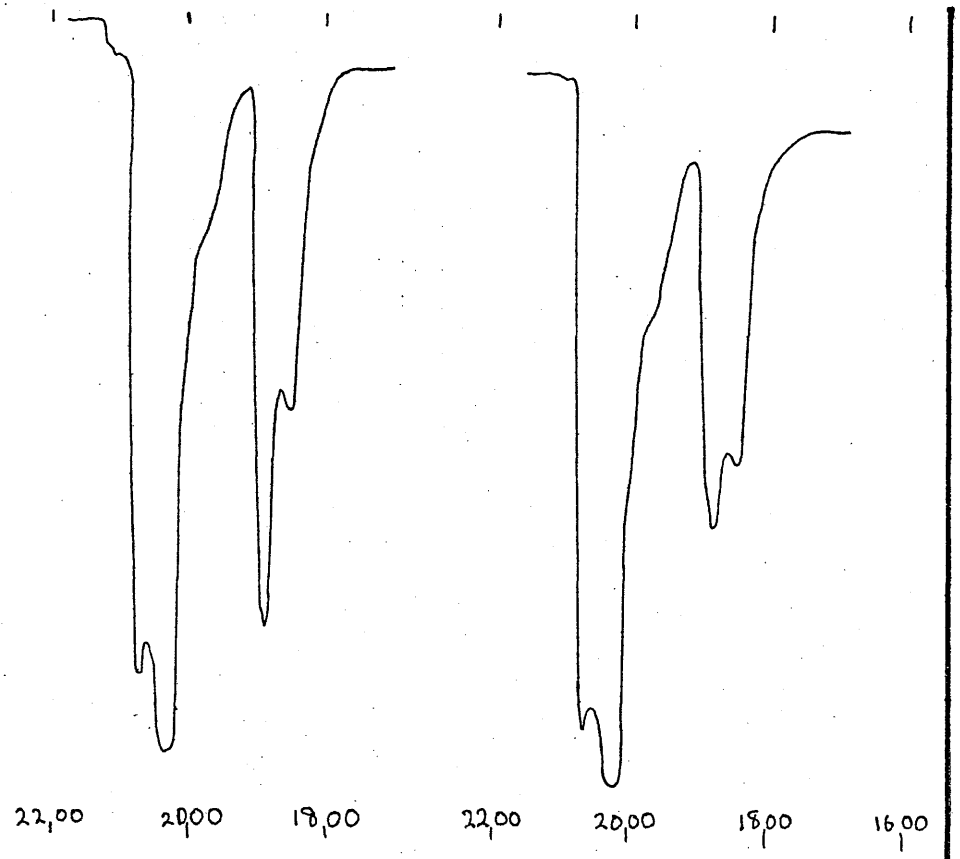


Figure 2.18

The reaction was repeated under nitrogen and gave very interesting i.r. spectra. The reaction was half way finished after four hours with further progress to complete conversion being made overnight. The interest lay in the carbonyl stretches observed in the 1900-2100 cm^{-1}. These were assigned to a mixture $Co_2(CO)_8$, $Co_4(CO)_{12}$ and $[Co_3(CO)_{10}]^-$ in solution, in addition to $[Co(CO)_4]^-$. The inference is that under nitrogen, carbonyl deficient species can form, this mode of reaction being unlikely under carbon monoxide. After being left for a few days, the reaction stabilised with $Co_4(CO)_{12}$, $[Co_3(CO)_{10}]^-$ and $[Co(CO)_4]^-$ in equilibrium (see Fig. 2.20, i.r. run on Perkin Elmer, (P.E.) 257).

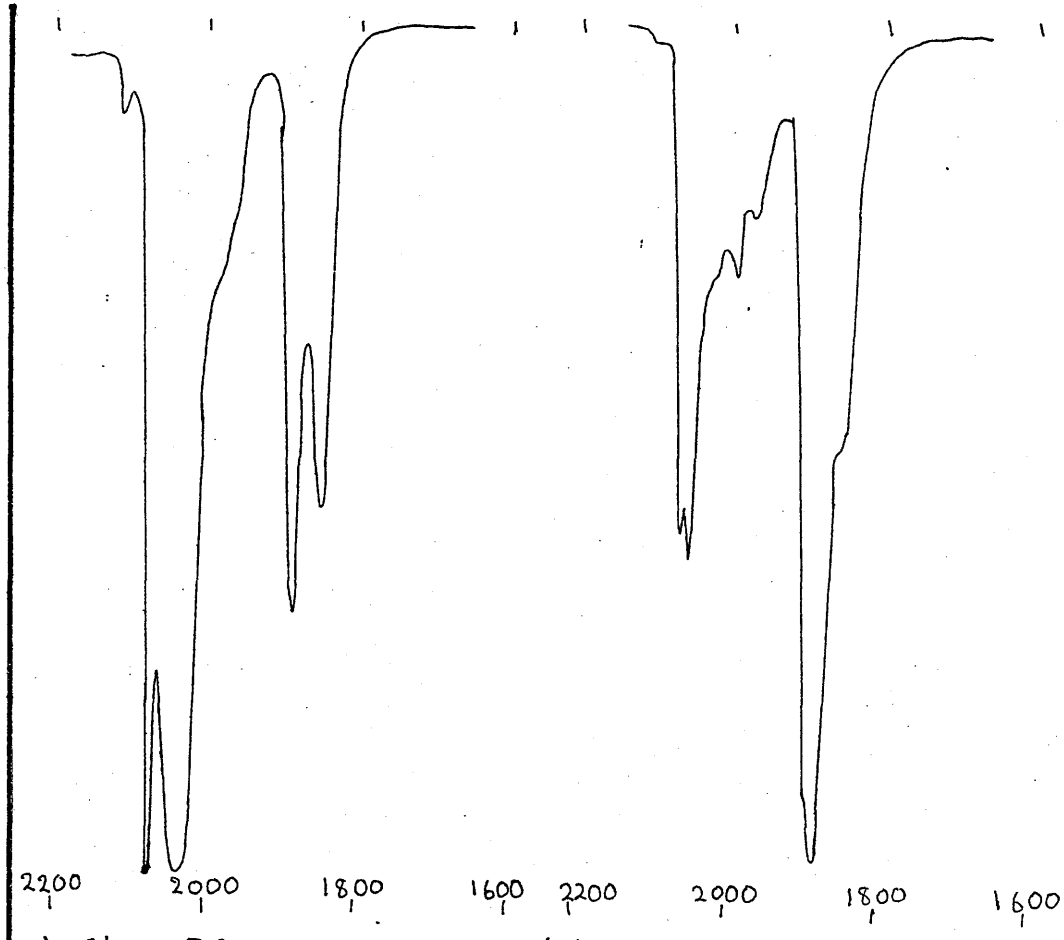
With the exception of $[BH_4]^-$, the anions tested did not compare favourably with the free halides. This is partly due to poor solubility and partly to the low nucleophilicity of the reagent.

Next on the agenda was a series of bromide compounds. Sodium bromide, NaBr, gave complete conversion to $[Co(CO)_4]^-$ in five - ten minutes when used in a carbon monoxide environment with the usual stoichiometry. Under nitrogen however complexity again reigned supreme. After two hours most of the cobalt carbonyl species in solution was $[Co(CO)_4]^-$, along with some $Co_2(CO)_8$, a little $[Co_3(CO)_{10}]^-$ and traces of $Co_4(CO)_{12}$ (the presence of the latter is required to explain the changes in the i.r. spectrum, at the terminal region, of $Co_2(CO)_8$) - see Fig. 2.21a. The reaction went to completion in under twenty hours to give $[Co(CO)_4]^-$ with a shoulder at 1860 cm^{-1} in the i.r. spectrum. (see Fig. 2.21b). Both i.r. spectra were from the P.E. 257 spectrometer. As will be demonstrated later, this modified spectrum of $[Co(CO)_4]^-$ is due to the perturbation by the cation under rigorous anhydrous conditions. The large concentration of $[Co(CO)_4]^-$ present in solution accounts for the shoulder being easily observed.



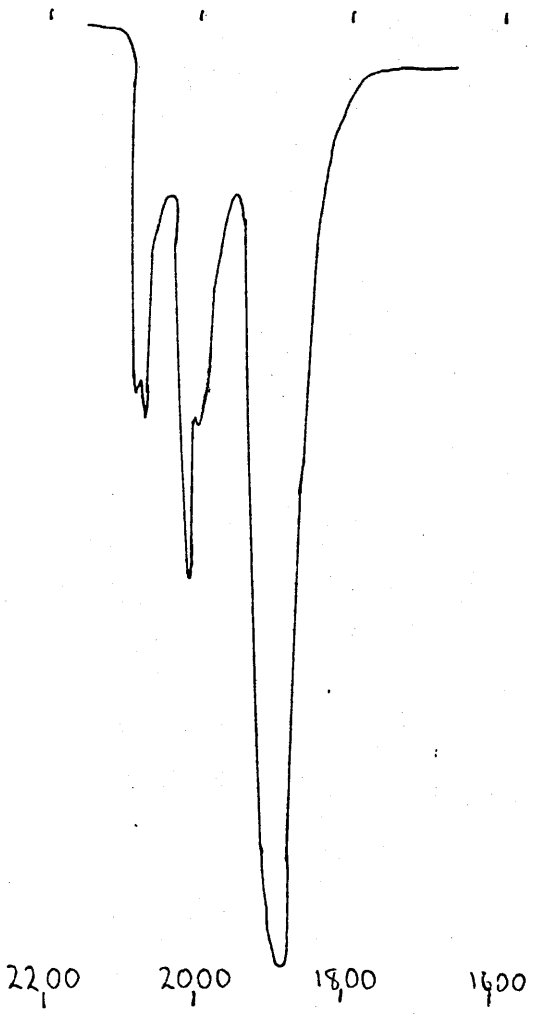
a) after 3days b) after 30hrs

Figure 2.19 [see text]



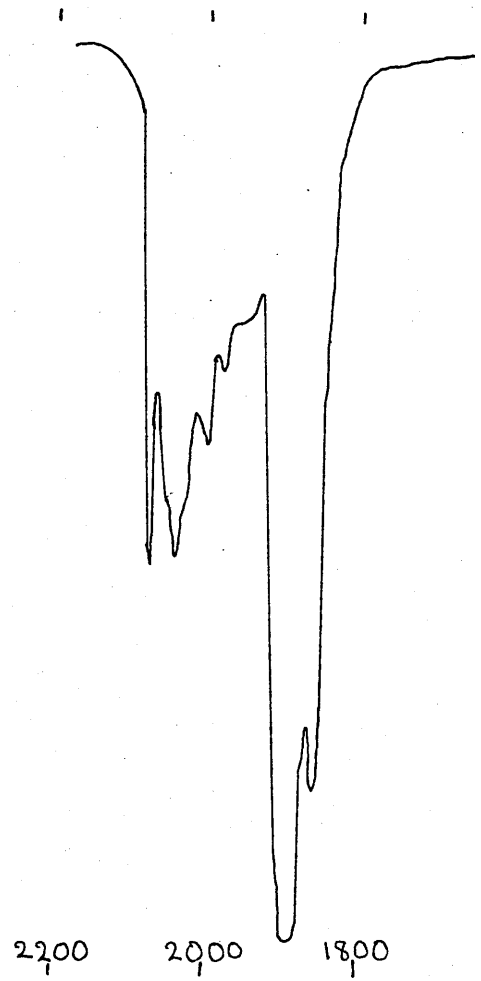
a) after 30mins b) after 22½ hrs

Figure 2.20

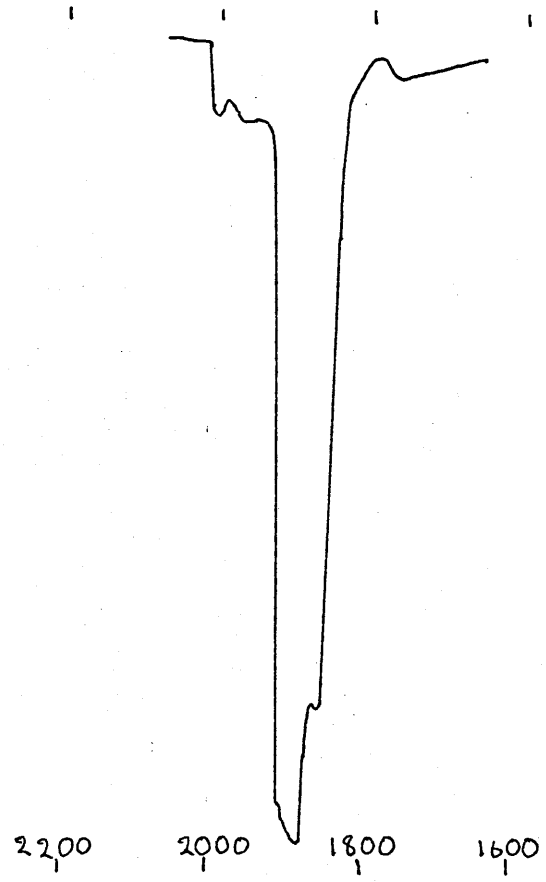


c) after 3days

Figure 2,20[cont]



a) after 70 mins



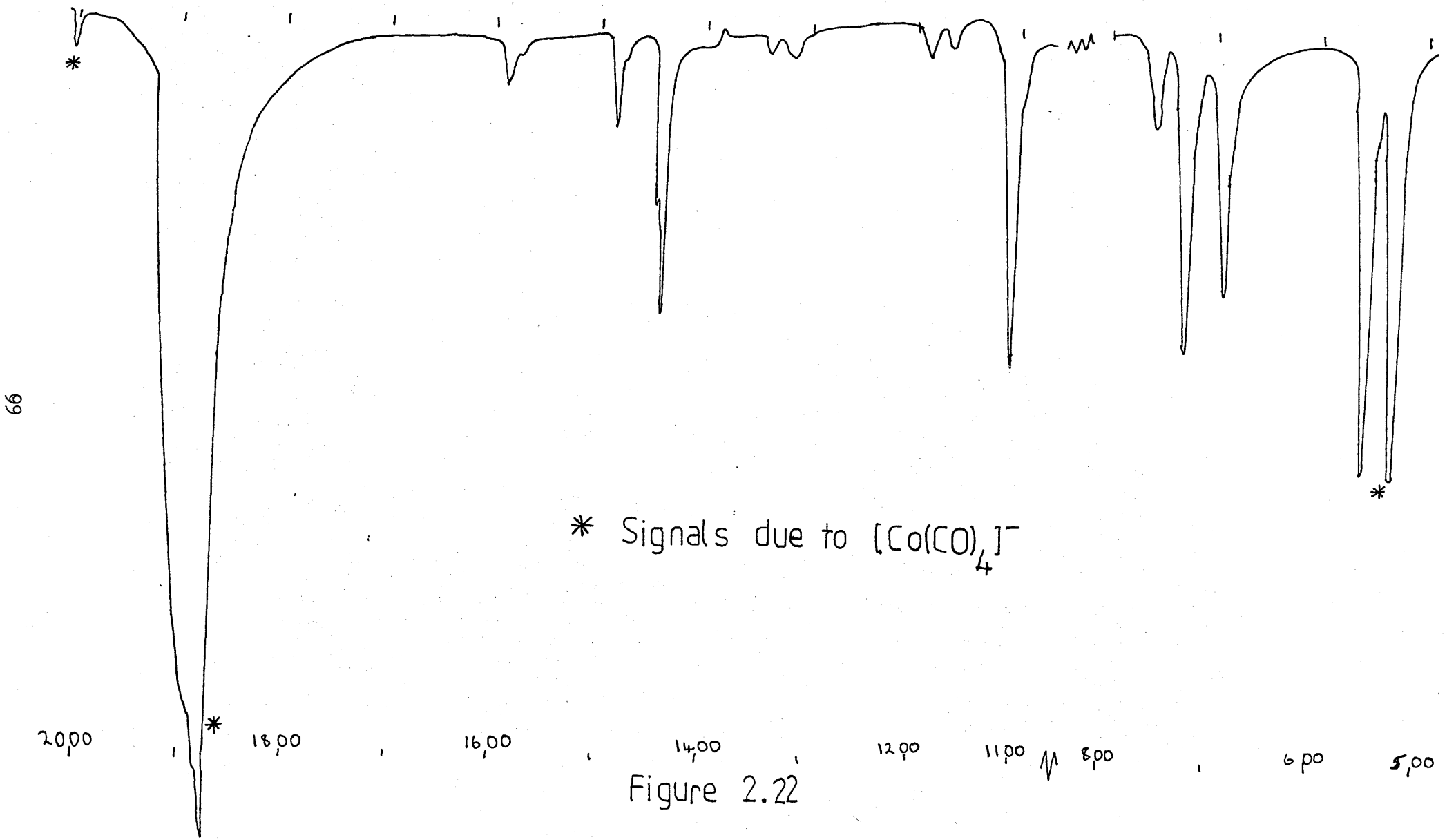
b) after 19 hrs

Figure 2.21

Tetrabutylammonium bromide, $n\text{-}Bu_4NBr$, was found to react in the accepted manner although over a longer period of time. The reaction proceeds smoothly under carbon monoxide in thirty - sixty minutes. An attempt to isolate the salt $[n\text{-}Bu_4N][Co(CO)_4]$ from solution was made, after establishing that large organic cations would stabilise $[Co(CO)_4]^-$, but these were unsuccessful, the solid isolated decomposing rapidly to a black tarry sludge. Tetrabutylphosphonium bromide, $n\text{-}Bu_4PBr$, was found to mimic the $[n\text{-}Bu_4N]^+$ compound very closely in its reactions with $Co_2(CO)_8$.

Using the bulkier reagent tetraphenylphosphonium bromide, Ph_4PBr, led to surprising results. Complete reaction was found after ten - fifteen minutes in a carbon monoxide atmosphere (although higher concentrations of Ph_4PBr and $Co_2(CO)_8$ take longer to go to completion because of the rate of Ph_4PBr dissolving in T.H.F.). On working up the dark green solution, a pale green solid was isolated which proved to be tetraphenylphosphonium tetracarbonylcobaltate (-1) $[(Ph_4P)^+ \{Co(CO)_4\}^-]^-$ Fig. 2.22.

This compound is capable of being handled for some minutes in the air but prolonged exposure leads to decomposition, noticeable by the change in colour to a black solid through a dark green stage. It could prove a useful method of storing the anion in a solid form for future use, as will be demonstrated later (in chapter 6), but remaining soluble in organic solvents. Addition of iodomethane, MeI, to this solution should give the alkyl species $MeCo(CO)_4$. From the literature, this is formed by $NaCo(CO)_4$ and MeI reacting in T.H.F. or diethyl ether at 0^oC, then being cooled to -30^oC. This will undergo decomposition to give 2-propanone, $Co_2(CO)_8$ and $Co_4(CO)_{12}$ on being allowed to warm up to room temperature[150]. This was attempted, at 0^oC, and gave a reproducible complex spectrum after fifteen minutes - Fig. 2.23a. The higher



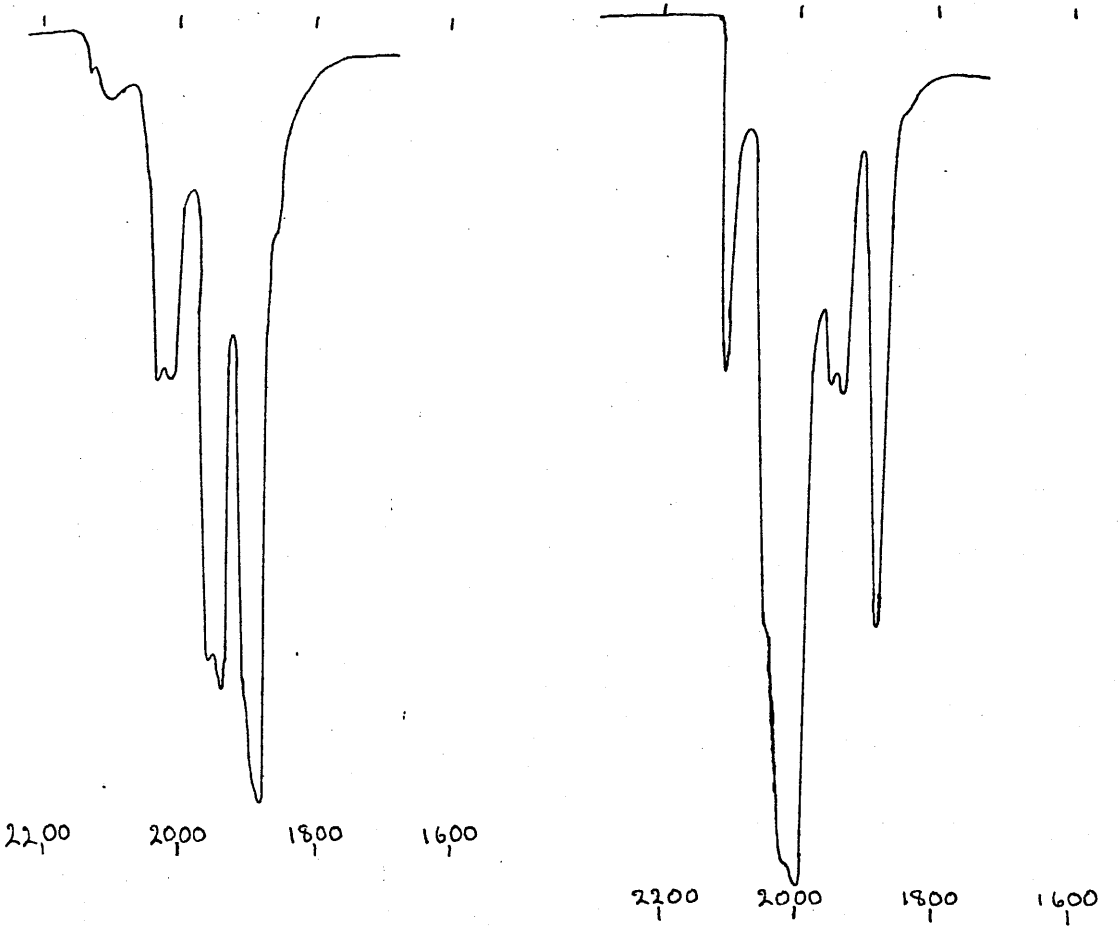
* Signals due to $[Co(CO)_4]^-$

Figure 2.22

frequency signals can be assigned to $Co_4(CO)_{12}$, the signal at 1880 cm^{-1} is the anion. As time passed the solution lightened in colour and the i.r. spectrum increased in complexity. Within two hours, the spectrum below (Fig. 2.23b) was obtained.

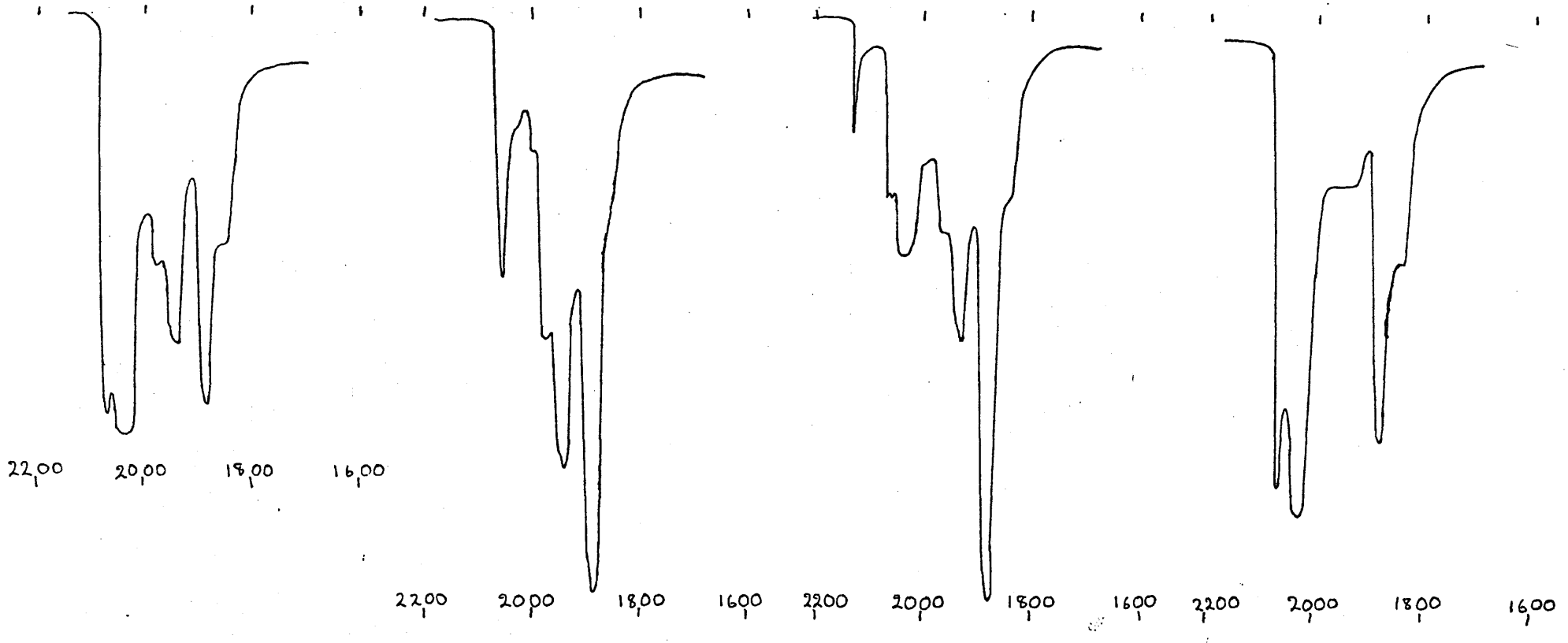
The bands at 2000 cm^{-1} are a mixture of $Co_4(CO)_{12}$ and an alkylcobalt species, $MeCo(CO)_4$ (?), or a similar acyl species (lit. values in hexane of $MeCo(CO)_4$ - 2105, 2035 and 2019 cm^{-1} [226]) with $[Co(CO)_4]^-$ in lower concentration at 1880 cm^{-1}. On heating to room temperature the solution yields 2-propanone (i.r. band at 1720 cm^{-1}) as expected along with a little of terminal cobalt carbonyl species (not assigned) - Fig. 2.23c.

Finally reactions of $Co_2(CO)_8$ with cobalt dibromide, $CoBr_2$, in T.H.F. were studied. Under carbon monoxide the reaction took 48 hours to produce more than 50% of anion in solution, suspected to be largely due to the effect of T.H.F. The initial low concentration of anion formed within half an hour persisted at that level for twenty four hours. Varying the ratio of $CoBr_2$:$Co_2(CO)_8$ did not affect rate of anion production. Under nitrogen, yet again, a different story emerges. Within half an hour an appreciable amount of anion had appeared in addition to $Co_2(CO)_8$ in solution and a new mystery species, absorbing at 1940 cm^{-1}. This is tentatively assigned as $Co_2(CO)_7.THF$. (i.e. 1 mole of T.H.F. replacing a terminal CO group). - see Fig. 2.24a. The effect of the passage of a further one and a half hours was to create the anion as the dominant species (Fig. 2.24b), this state of affairs remaining constant over two days. A carbon monoxide atmosphere at this stage leads to further reaction within the hour (Fig. 2.24c), with a static situation being reached after another two hours in which both $Co_2(CO)_8$ and $[Co(CO)_4]^-$ are present (Fig. 2.24d).



a) after 15 mins b) after 2hrs c) after 25hrs

Figure 2.23



a) after 25mins b) after 2hrs c) after 40mins d) after 3hrs

Figure 2.24 [see text]

It is obvious that the choice of experimental atmosphere will determine the products of reaction, in situations where 100% conversion is not achieved. Several schemes, outlined in Figs. 2.25 and 2.26 could apply, under various conditions:

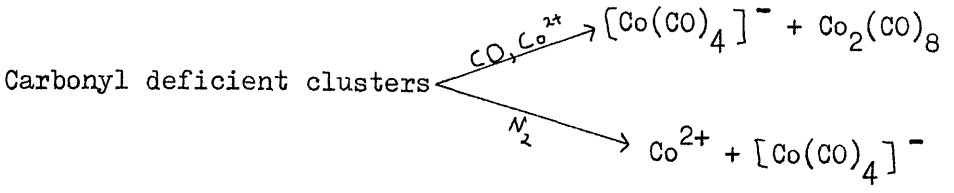


Figure 2.25

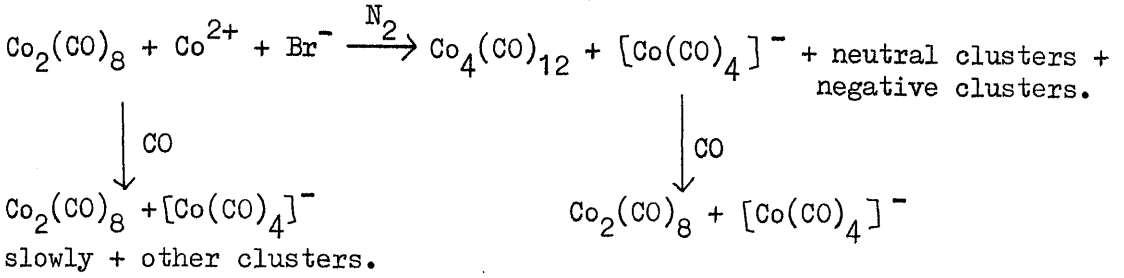


Figure 2.26

This can be summarised by the equilibria of equation 2.32:

$$Co_2(CO)_8 \underset{CO}{\overset{N_2}{\rightleftharpoons}} \text{carbonyl deficient cobalt carbonyls} \xrightarrow{N_2} \text{cluster species (A)} \qquad (2.32)$$

(A) in the presence of $[Co(CO)_4]^-$ will undergo further reaction, under CO, possibly via an intermediate cluster, giving $Co_2(CO)_8$.

It was confirmed that Co^{2+} (as $CoBr_2$) will not react with carbon monoxide. One idea mooted as the reason for slow disproportionation under certain circumstances was a poisoning effect of Co^{2+} (either by itself or by acting as a halide 'sink' effectively removing the catalyst from solution). To see if Co^{2+} itself poisoned the reaction, a cobaltous salt with a bulky anion was used. Cobaltous bistetrafluoroborate, $[Co(BF_4)_2.THF_x]$, was chosen, prepared and added to a solution of $Co_2(CO)_8$ in T.H.F. under carbon monoxide. The experiment was run against a blank, i.e. $Co_2(CO)_8$ in T.H.F. to isolate the effect of solvent itself. Within an hour slight traces of anion could be observed in the main reaction (see Fig. 2.27a) which grew very slowly to the stage shown in

Fig. 2.27b after thirty hours. At this stage in the blank experiment only traces of $[Co(CO)_4]^-$ were present (Fig. 2.27c). Switching the main experiment to nitrogen increased the $[Co(CO)_4]^-$ concentration dramatically within half an hour (Fig. 2.27d) with loss of $Co_2(CO)_8$ (initially some $Co_4(CO)_{12}$ was formed but this too disappeared from solution) until only $[Co(CO)_4]^-$ was present, after twelve hours. Adding $[Co(BF_4)_2, T.H.F._x]$ to $[Co(CO)_4]^-$ (present as $[Ph_4P]^+[Co(CO)_4]^-$ in T.H.F.) under either nitrogen or carbon monoxide had no effect. It was concluded that Co^{2+} itself did not poison the reaction, thus it was the removal of free halide from solution that inhibited reaction. The effect of T.H.F. itself on $Co_2(CO)_8$ under nitrogen was studied and again cobalt carbonyl deficient species were detected. Initially the only other species present is $[Co(CO)_4]^-$ but $Co_4(CO)_{12}$ is formed within the hour (Fig. 2.28a). Reaction after twenty four hours gives $Co_4(CO)_{12}$ and $[Co(CO)_4]^-$ as the only complexes present (Fig. 2.28b) which slowly combine to give $[Co_3(CO)_{10}]^-$ in addition to themselves (Fig. 2.28c). These spectra were run on the P.E.257 spectrometer, and are shown overleaf.

This reaction is summarised in Fig. 2.29

$$Co_2(CO)_8 + \text{T.H.F. in Nitrogen}$$
$$\downarrow \text{10 min.}$$
$$Co_2(CO)_8 + [Co(CO)_4]^-$$
$$\downarrow \text{1 hr. 20 min.}$$
$$Co_2(CO)_8 + Co_4(CO)_{12} + [Co(CO)_4]^-$$
$$\downarrow \text{overnight.}$$
$$Co_4(CO)_{12} + [Co_3(CO)_{10}]^- + [Co(CO)_4]^-$$

Figure 2.29

The products of the above reactions are tabulated below, for ease of reference.

Reactions of $Co_2(CO)_8$ with Various Catalysts in T.H.F., after 24 Hours.

Catalyst	Products formed under Nitrogen	Products formed under Carbon Monoxide
LiBr	$[Co(CO)_4]^-$	$[Co(CO)_4]^-$
NaBr	$[Co(CO)_4]^-$	$[Co(CO)_4]^-$
Bu_4NBr	N/A	$[Co(CO)_4]^-$
Bu_4PBr	N/A	$[Co(CO)_4]^-$
Ph_4PBr	N/A	$[Co(CO)_4]^-$
$LiBH_4$	N/A	$[Co(CO)_4]^-$
$LiBF_4$	N/A	$[Co(CO)_4]^- + Co_2(CO)_8$
$LiPF_6$	$[Co(CO)_4]^- + Co_2(CO)_8 + Co_4(CO)_{12} + [Co_3(CO)_{10}]^-$ (?)	$[Co(CO)_4]^- + Co_2(CO)_8$
$CoBr_3$	$[Co(CO)_4]^- + Co_2(CO)_8 + Co_2(CO)_7(THF)$(?)	$[Co(CO)_4]^- + Co_2(CO)_8$
$Co(BF_4)_2$	$[Co(CO)_4]^-$ + traces of $Co_4(CO)_{12}$	$[Co(CO)_4]^- + Co_2(CO)_8$
- (low concn.)	$[Co(CO)_4]^- + Co_4(CO)_{12}$	$[Co(CO)_4]^- + Co_2(CO)_8$
- (high concn.)	$Co_4(CO)_{12}$	no reaction

Using diglyme or glyme as the solvent and LiBr as the catalyst leads to faster disproportionation than in T.H.F., within five minutes.

N/A Not Available.

Table 2.4

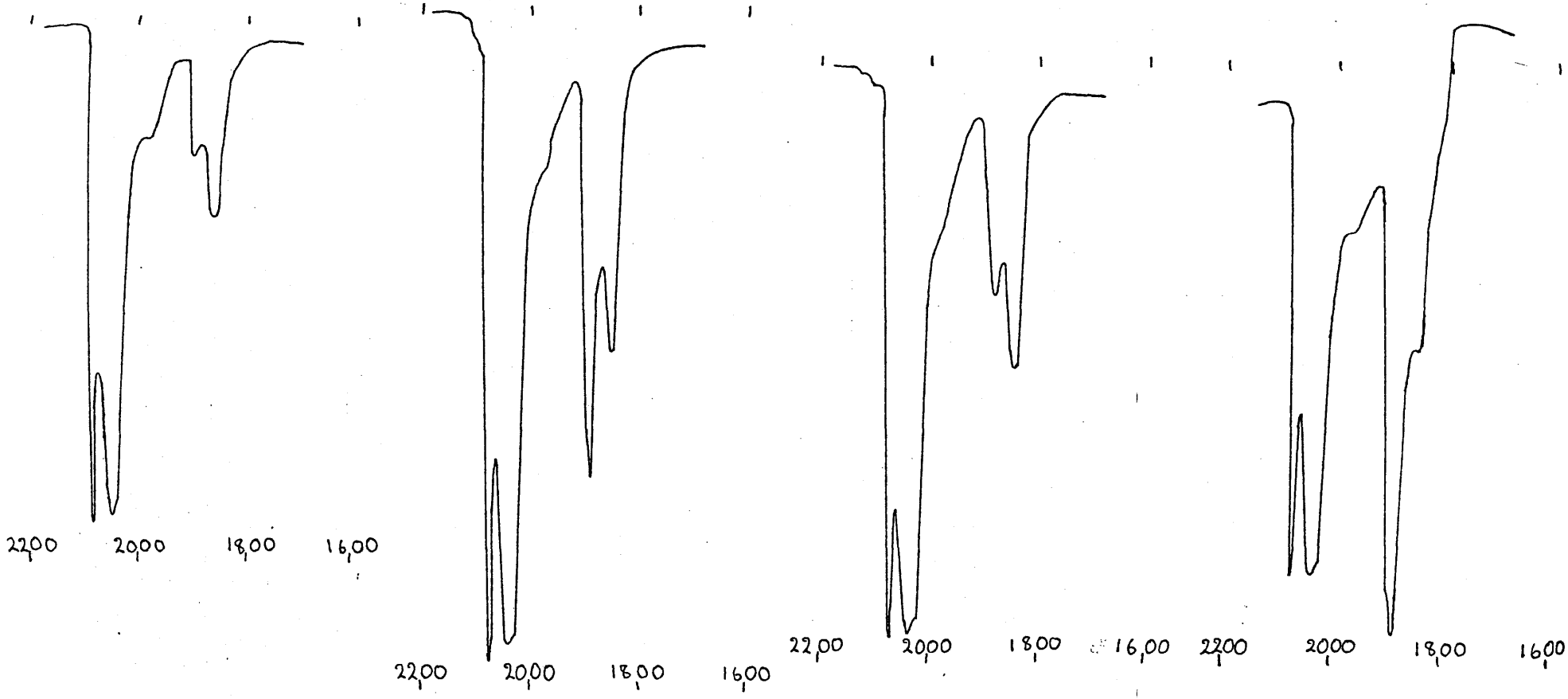
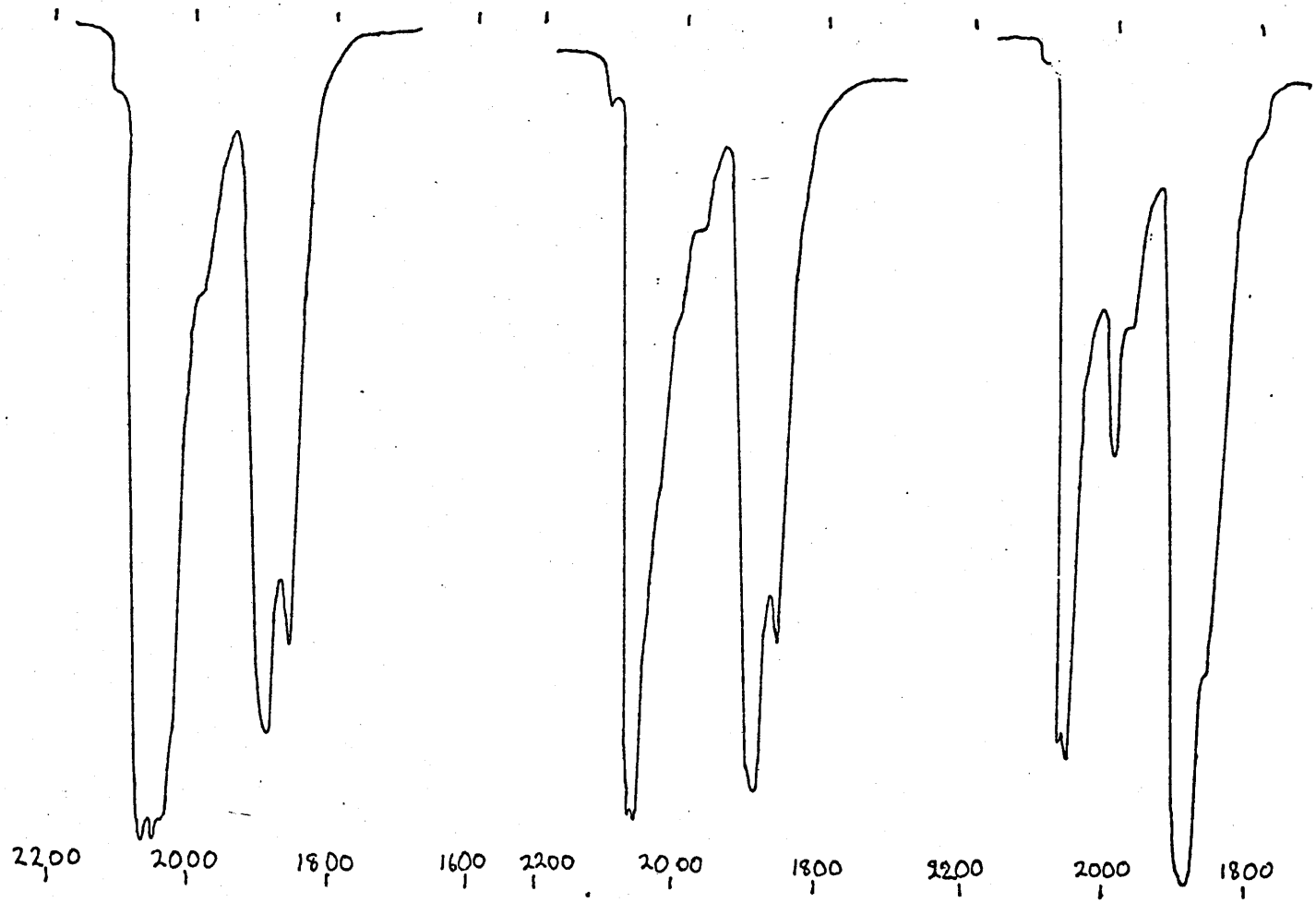


Figure 2.27 [see text]



a) after 85 mins b) after 23hrs d) after 2days

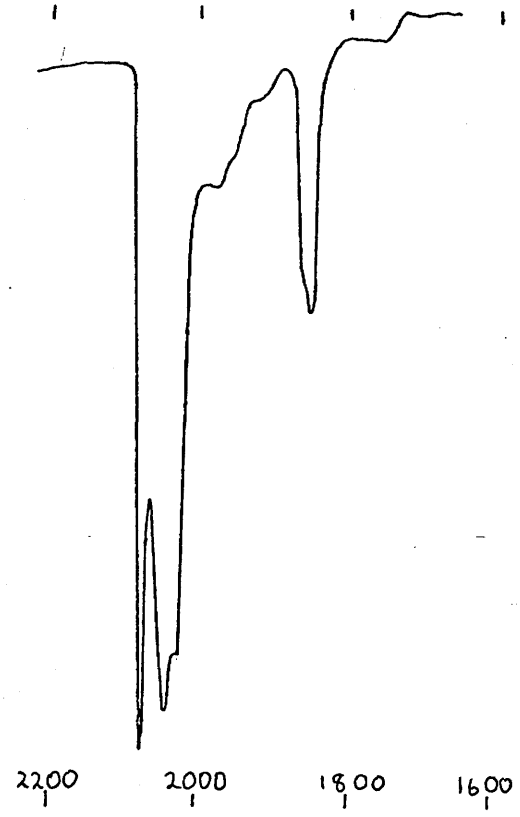
Figure 2.28

3. HALIDE INDUCED DISPROPORTIONATION OF $Co_2(CO)_8$ IN DIETHYL ETHER AND ITS REACTIONS.

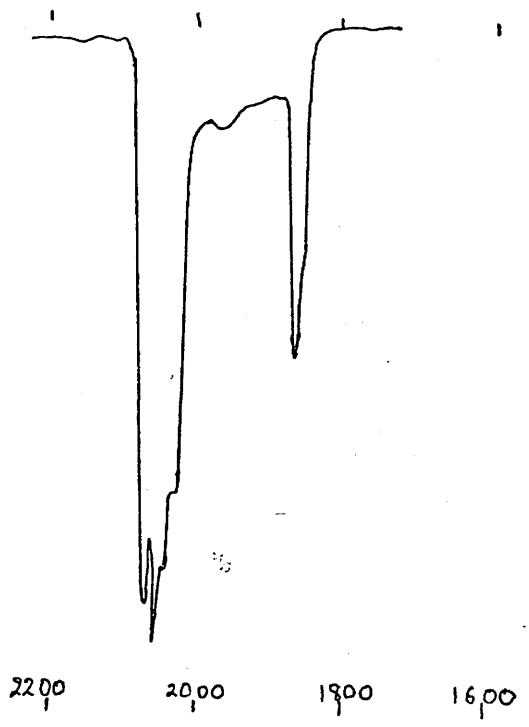
Diethyl ether enjoys certain advantages over T.H.F.; it is a poorer donor solvent (and so less likely to form adducts); it is easy to remove (because of its low boiling point) and it does not have such a high affinity for water. This combined to make it an attractive proposition as a solvent for halide induced disproportionation, and so use it we did. The first drawback was not long in presenting itself. On addition of $Co_2(CO)_8$ to diethyl ether, under carbon monoxide, a similar simple explicable i.r. spectrum of $Co_2(CO)_8$ in T.H.F. was not observed; rather the terminal carbonyl stretches were modified. When left to its own devices for a couple of hours further "modification" had occurred with the signal at 2040 cm^{-1} becoming less intense, which considerately remained constant over the next twenty four hours (Fig.2.30a). The experiment was repeated using nitrogen as an atmosphere which, as already demonstrated, only proceeded to complicate matters further. Initially an i.r. spectrum resembling Fig. 2.30a was noted but after the elapse of one hour, signals attributed to $Co_4(CO)_{12}$ were observed, (Fig. 2.30b and c) which did not change overmuch in the next few hours (Fig. 2.30d). Spectra shown in Fig. 2.30 were all from runs on the P.E.257 spectrometer.

A plot of log (I_o/I) vs time was constructed and is shown in Fig.2.31, with assignments, but did not prove very helpful.

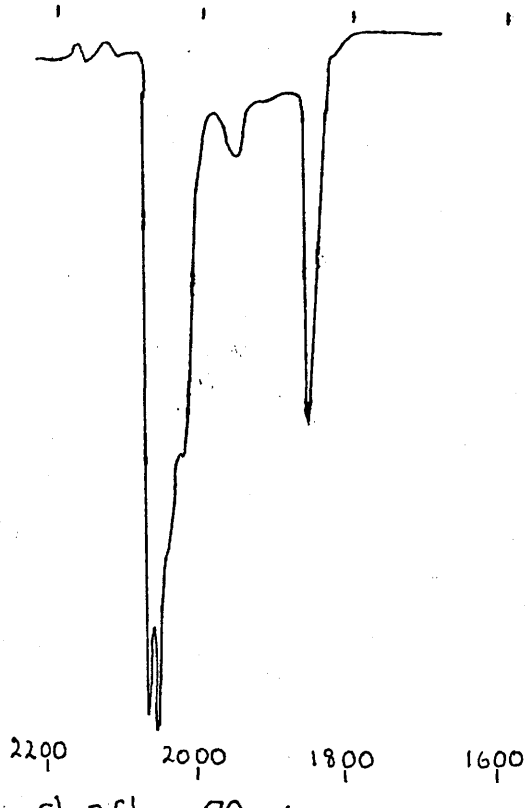
Not daunted it was agreed to form $[Co(CO)_4]^-$ using LiBr and $Co_2(CO)_8$ in diethyl ether under carbon monoxide. As in the T.H.F. experiment, there were indications of a reaction within five minutes, but not formation of the anion. The i.r. spectrum obtained after twenty minutes remained unchanged for the first hour (Fig. 2.32a) and after ninety hours had not altered significantly. Fig. 2.32b shows the i.r.



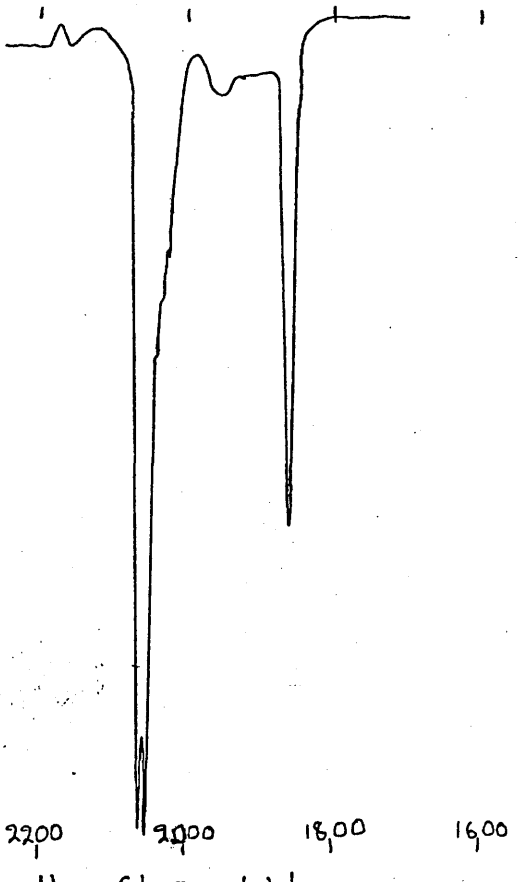
a) after 22hrs



b) after 30mins



c) after 70 mins



d) after 4½hrs

Figure 2.30 [see text]

Assignments for Fig. 2.31

	$\tilde{\nu}$ (cm^{-1})	Assignment (Terminal $\tilde{\nu}$ (CO) unless stated)
a	2060	$Co_2(CO)_8$
b	2030	$Co_2(CO)_8$
c	2015	$Co_2(CO)_8$
d	1950	Solvent
e	1910	Solvent / Impurity?
f	1845	Bridging carbonyl - $Co_2(CO)_8$ and $Co_4(CO)_{12}$
g	1855	Bridging carbonyl $Co_4(CO)_{12}$
h	2040	$Co_4(CO)_{12}$
j	2055	$Co_4(CO)_{12}$
k	2020	$Co_2(CO)_8$

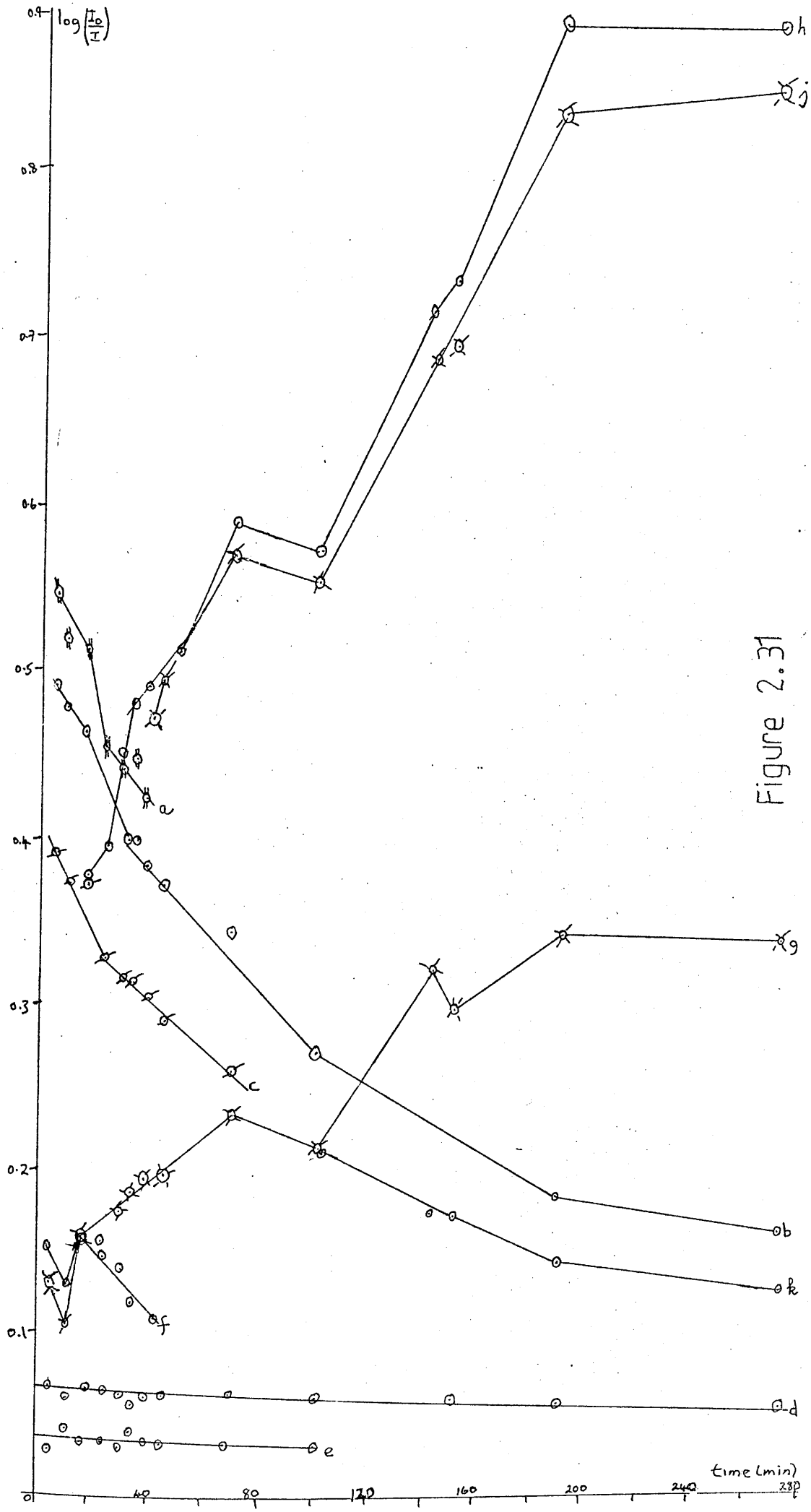

log(I0/I)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
40
80
120
160
200
240
280
time (min)
t
a
b
c
d
e
f
g
h
j
k

Figure 2.31

spectrum after ten days. The P.E.577 spectrometer was used for these i.r. spectra.

The work was repeated at $0^{o}C$ and using varying quantities of LiBr (between the range of zero to three lithium atoms per cobalt atom, the 'normal' ratio being 4:3). These measures did not resolve the complexity of the solution; the former only slows down the rate of reaction, while the latter alters the ratio of the different species present in solution. Plots of $\log (I_o/I)$vs concentration of LiBr did not help, although plotting $\log (I_o/I)$vs time enabled certain frequencies to be recognised as behaving in a similar manner, i.e. they belonged to the same species (see Fig. 2.33).

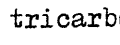
The $LiCo(CO)_4$ absorption in these experiments has moved from its usual position around 1880 cm^{-1} to 1910 cm^{-1}, demonstrating the effect of solvent on i.r. absorptions (c.f. $[Co(CO)_4]^-$ in H_2O which absorbs at 1919 cm^{-1} [205]). With hindsight, the other species in solution were:

$Co_2(CO)_8$ (c.f. Fig.2.30a): $\bar{\nu}$ (CO) 2070m, 2040m, 1860m

$[Co_3(CO)_{10}]^-$: $\bar{\nu}$ (CO) 2005s, 1995s, 1970m, 1860m

Using nitrogen as the reaction atmosphere serves to promote the formation of $Co_4(CO)_{12}$ and traces of other cobalt carbonyl species.

Using lithium iodide, LiI, instead of the bromide salt, gave similar results under carbon monoxide; under nitrogen a preference for a mixture of $Co_4(CO)_{12}$, $[Co_3(CO)_{10}]^-$ and a little anion was shown (Fig. 2.34, using the P.E.577 spectrometer).

To confirm that the anion was present in solution (i.e. the assignment of the 1910 cm^{-1} signal was correct) allyl bromide was added to the solution. In T.H.F., $[Co(CO)_4]^-$ will react with allyl bromide to give the complex π allylcobalt tricarbonyl,  , with a characteristic i.r. spectrum (Fig. 2.35a) of $\bar{\nu}$(CO): 2068, 2000 cm^{-1}.

To isolate an air stable derivative excess triphenyl phosphine, Ph_3P,

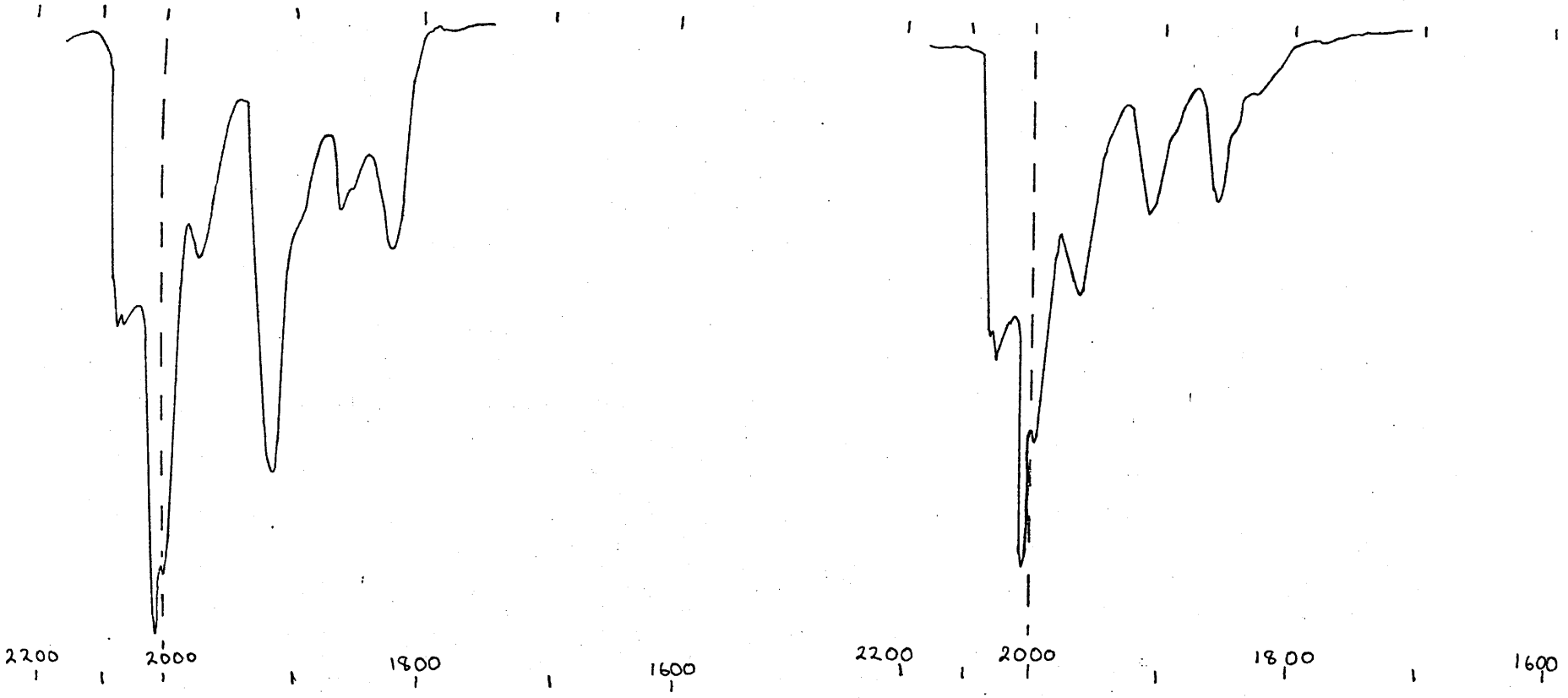

2200
2000
1800
1600
a) after 30mins
2200
2000
1800
1600
b) after 10 days

Figure 2.32

Assignments for Fig. 2.33

	$\tilde{\nu}$ (cm^{-1})	Assignment (Terminal $\tilde{\nu}$(CO) unless stated)
a	2075	$Co_2(CO)_8$; $Co_4(CO)_{12}$?
b	2040	$Co_2(CO)_8$ and $Co_4(CO)_{12}$
c	2015	$Co_2(CO)_8$
d	1995	$Co_2(CO)_8$; $Co_4(CO)_{12}$? $[Co_3(CO)_{10}]^-$?
e	1850	Bridging carbonyls of neutral species and $[Co(CO)_4]^-$
f	1910	$[Co(CO)_4]^-$
g	2020	$Co_4(CO)_{12}$?

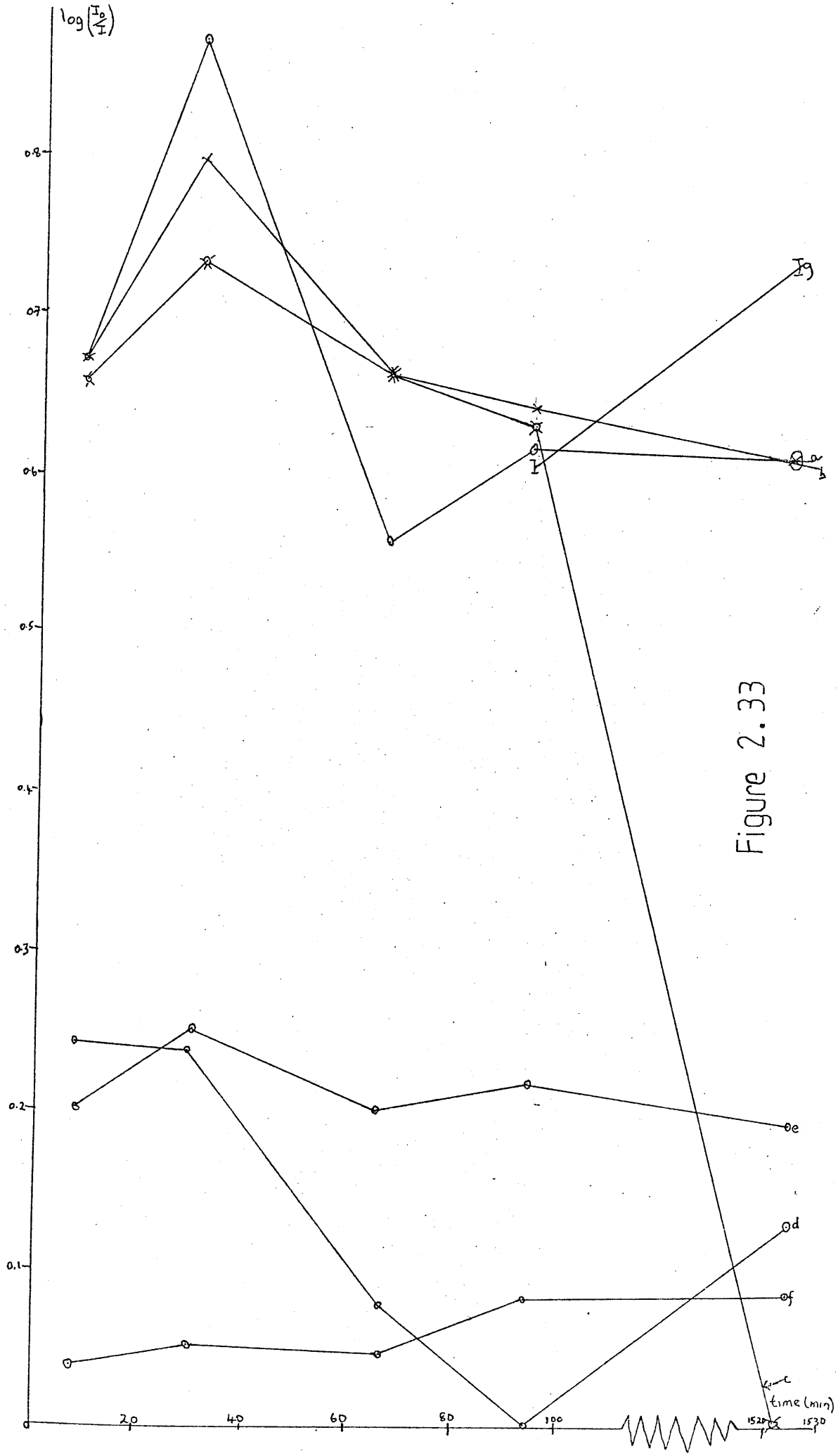
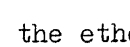
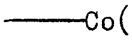

log(I0/I)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
20
40
60
80
100
1520
1530
time (min)
a
b
c
d
e
f
g

Figure 2.33

is added and π allylcobalt dicarbonyl triphenyl phosphine,  $Co(CO)_2(PPh_3)$, is formed ($\bar{\nu}$ (CO) 2000, 1948 cm^{-1} Fig. 2.35b). For the ether solution of the anion, containing some $[Co_3(CO)_{10}]^-$ (Fig. 2.35c), addition of allyl bromide led to formation of the allylcobalt species, as predicted, with some anion remaining (Fig.2.35d). The reaction was completed by adding Ph_3P to give the stable product (Fig. 2.35e). All spectra were recorded on the P.E. 577 spectrometer. The experiment was repeated adding allyl bromide to $Co_2(CO)_8$ which showed no inclination to react. When the reaction was reinforced with LiBr,  $Co(CO)_3$ was formed with Ph_3P causing the phosphorus substituted derivative to be produced. At no time in this reaction was there spectroscopic evidence of $[Co(CO)_4]^-$, giving rise to the belief that any formed is rapidly consumed by allyl bromide.

Next to be put on trial were the other lithium salts. Lithium hydroxide, LiOH, showed no reaction whatsoever, mainly because of its inability to dissolve in diethyl ether.

$LiBH_4$, under carbon monoxide, as in the T.H.F. experiment, gave a similar range of products as LiBr (i.e. a complicated spectrum resulted) at a slower rate with gas evolution, the i.r. spectrum observed after one hour persisting w.r.t. time. $LiBF_4$ did not react.

Under carbon monoxide $LiPF_6$ and $Co_2(CO)_8$ in diethyl ether showed modification of the terminal carbonyl region but otherwise showed no visible reaction after twenty four hours (Fig. 2.36a). Under nitrogen a similar effect was noted initially but overnight the only species in solution was $Co_4(CO)_{12}$ (Fig. 2.36b). This reaction led to formation of anion (present after ten minutes), then $[Co_3(CO)_{10}]^-$ and $Co_4(CO)_{12}$ (after one hour), with $Co_2(CO)_8$ present throughout the first two hours. (Fig. 2.36 c and d, both run on the P.E. 257 spectrometer).

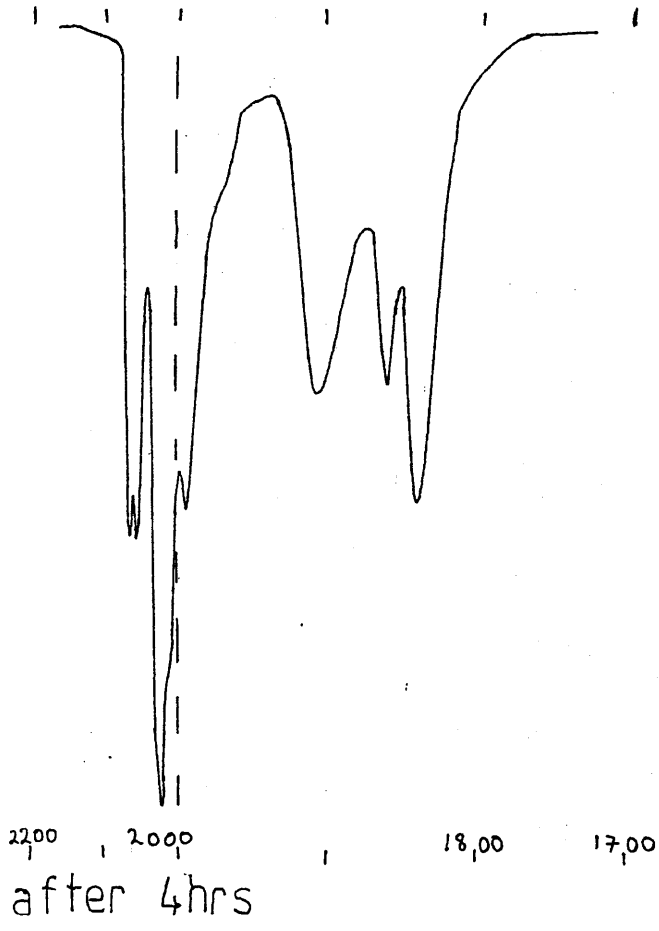


Figure 2.34

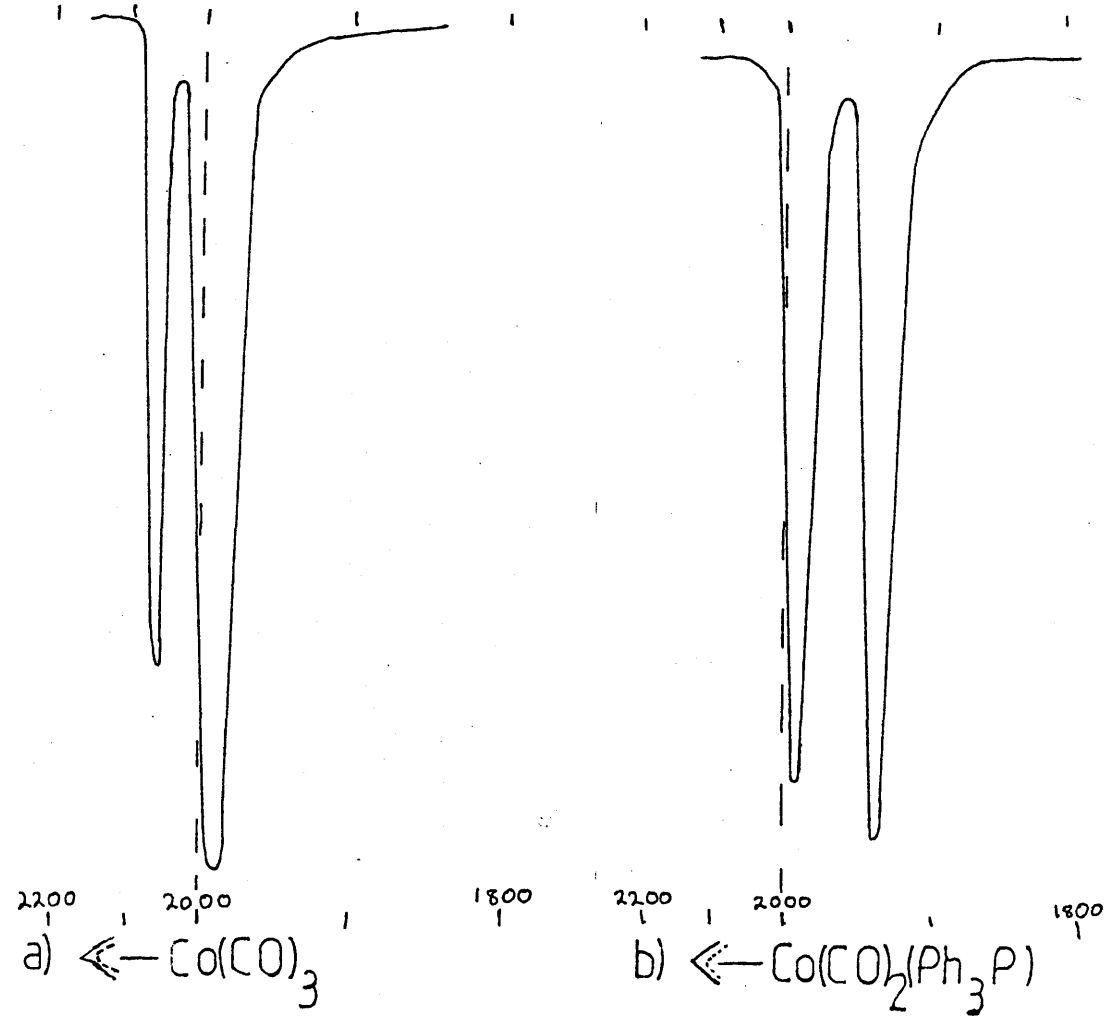
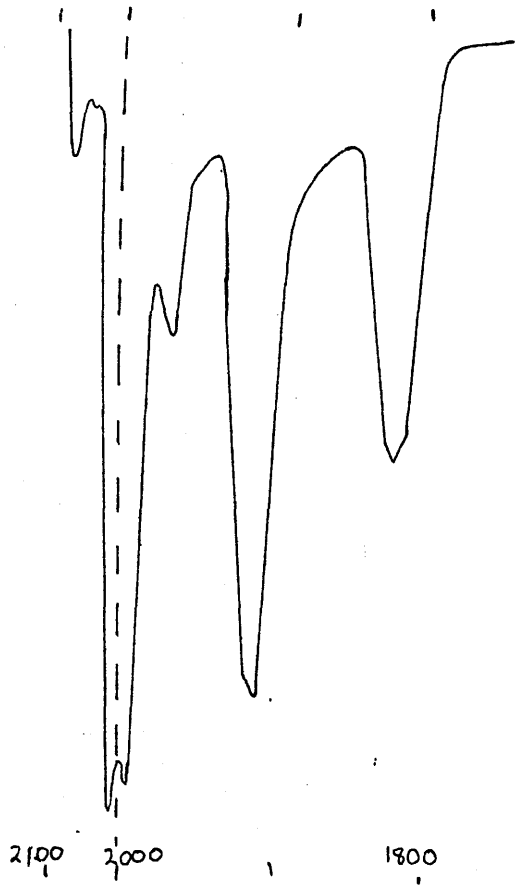
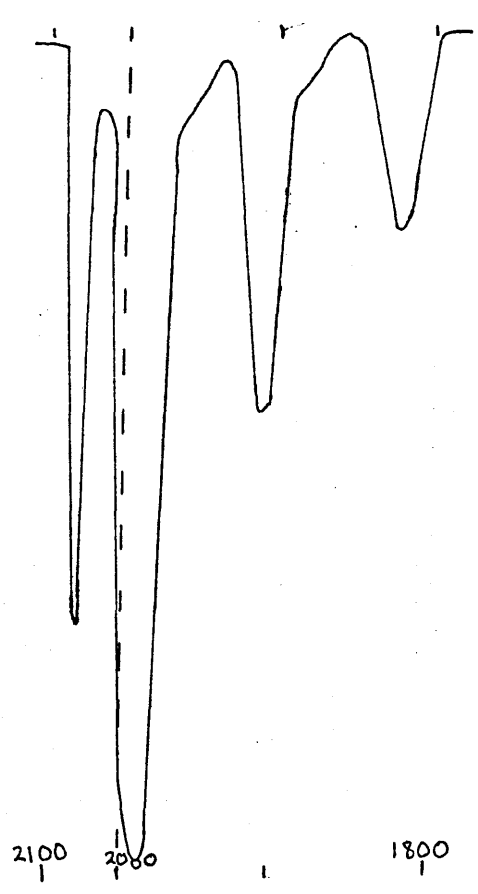


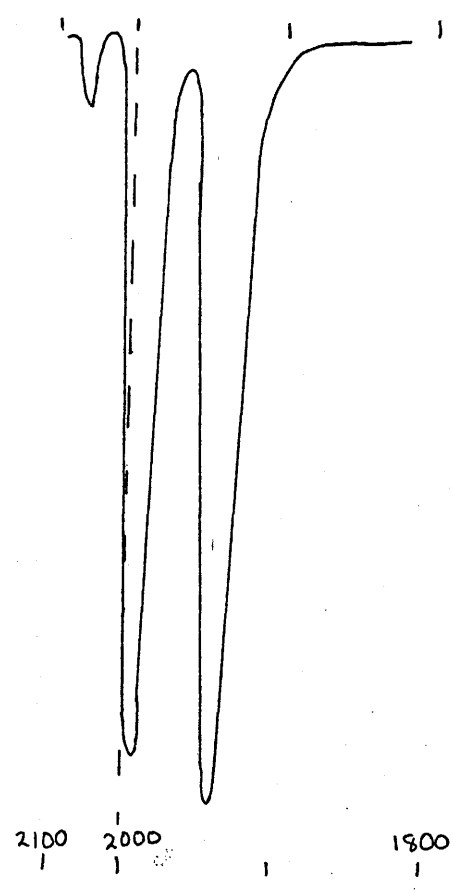
Figure 2.35



c) after 20mins

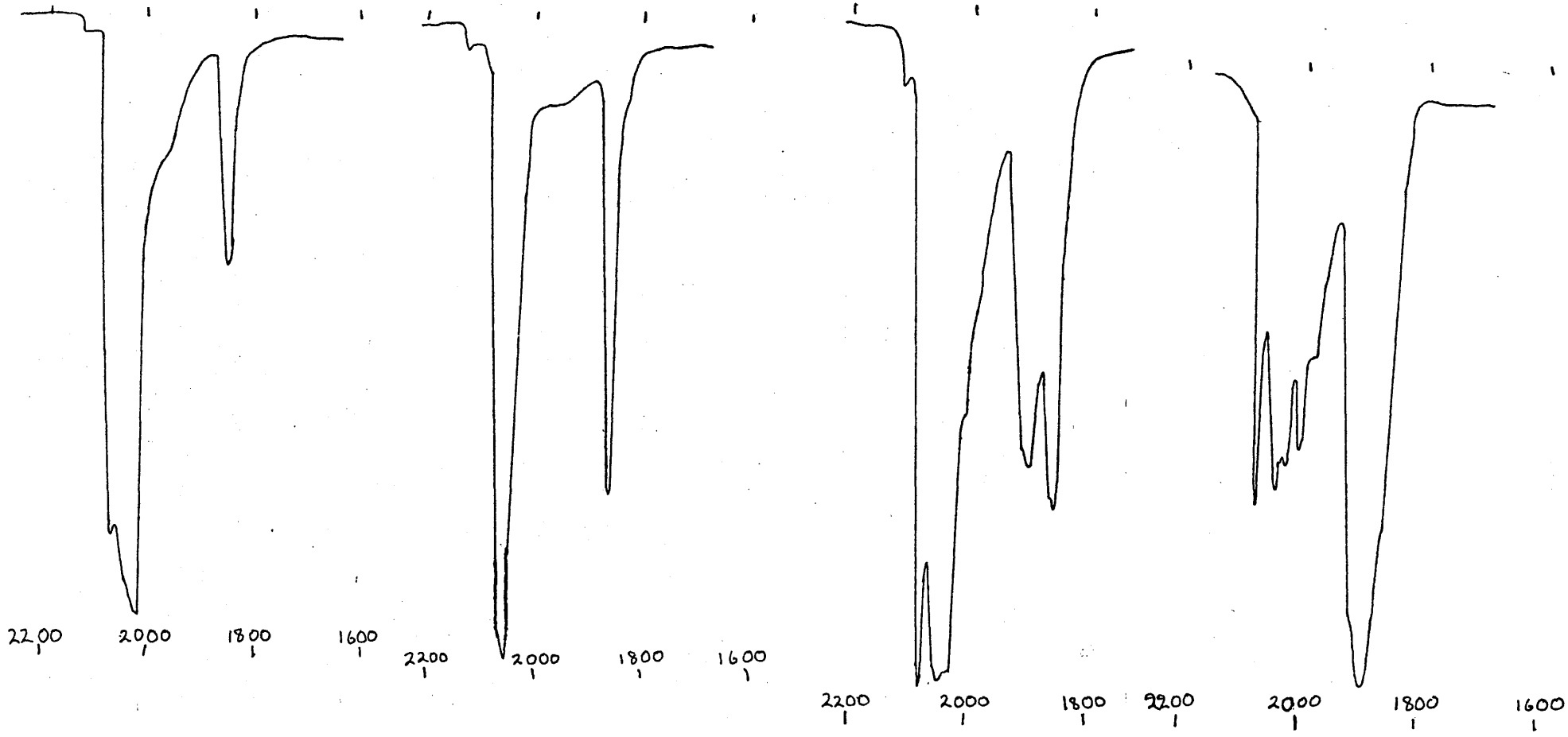


d) 30mins after allyl bromide added



e) 18hrs after Ph_3P added

Figure 2.35 [cont]



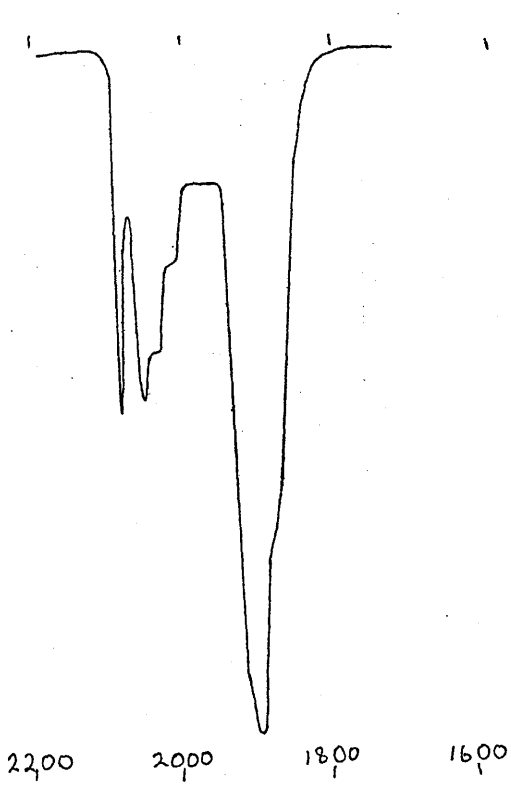
a) after 24hrs b) after 24hrs c) after 10 mins d) after 1hr

Figure 2.36 [see text]

Formation of the polar species $LiCo(CO)_4$ can be obtained by making the $NaCo(CO)_4$ compound, e.g. by sodium amalgam reduction and adding an excess of LiX (X = Br,I). This will be discussed in chapter 3. The work now moved on to other halide salts. NaBr, as anticipated, gave a complicated i.r. spectrum when added to $Co_2(CO)_8$ under carbon monoxide, but very slowly, requiring several days to reach the stage shown in Fig. 2.37 and a further day to have only $[Co(CO)_4]^-$ in solution. These observations are not solely due to reaction with solvent, as demonstrated by a blank experiment (i.e. $Co_2(CO)_8$ in diethyl ether, under carbon monoxide). Under nitrogen, reminiscent of previous experiments, $Co_4(CO)_{12}$ was the end product after three hours (the i.r. spectrum courtesy of the P.E. 257 spectrometer). $n\text{-}Bu_4NBr$, added to $Co_2(CO)_8$ in diethyl ether, under carbon monoxide tended to give simple spectra (c.f. LiBr situation), producing a blend of $Co_2(CO)_8$ and $[Co(CO)_4]^-$. Under nitrogen a mixture of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ was obtained.

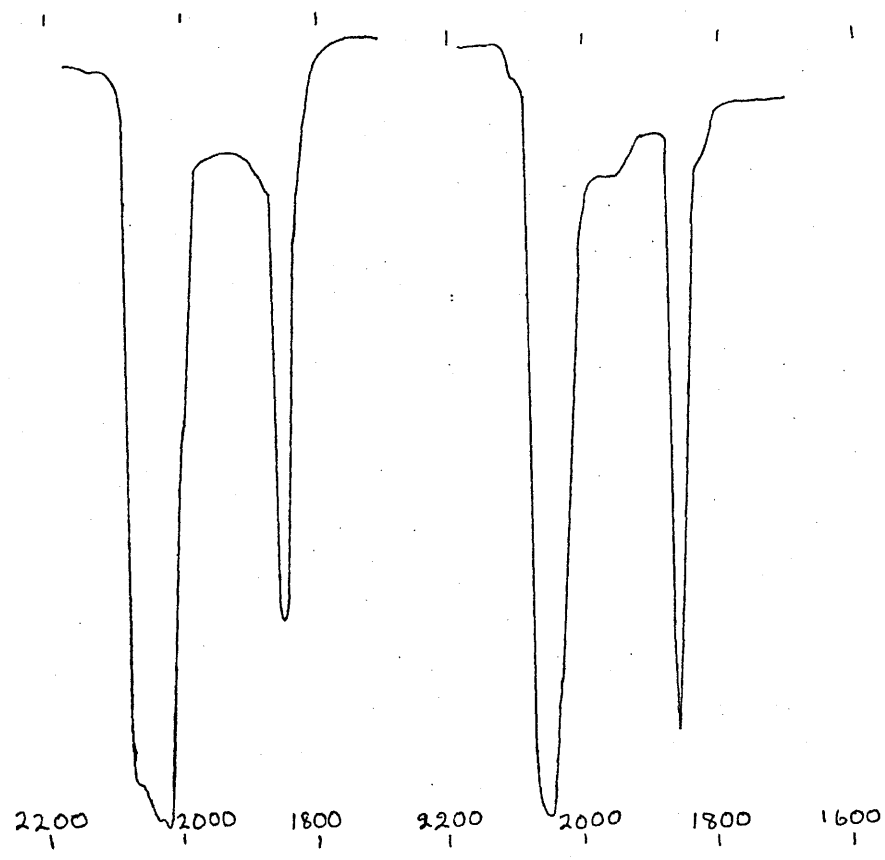
The only effect of Ph_4PBr upon the i.r. spectrum of $Co_2(CO)_8$ in diethyl ether, under carbon monoxide, was to decrease slightly the intensity of the signals over a period of three hours. Addition of $CoBr_2$ to this did not produce anything new, just hastened the disappearance of the old. It was then discovered that firstly Ph_4PBr is not terribly soluble in ethers and more importantly any anion being formed is immediately removed from solution as the insoluble ion pair $[Ph_4P]^+[Co(CO)_4]^-$.

To complete the set of halide salts, $CoBr_2$ was added to $Co_2(CO)_8$ in diethyl ether, under a) carbon monoxide and b) nitrogen. In the former reaction the only noticeable change in the spectrum was at the terminal carbonyl region, where possibly traces of $Co_4(CO)_{12}$ appear after twenty hours (Fig. 2.38a). For case b), as predicted, only



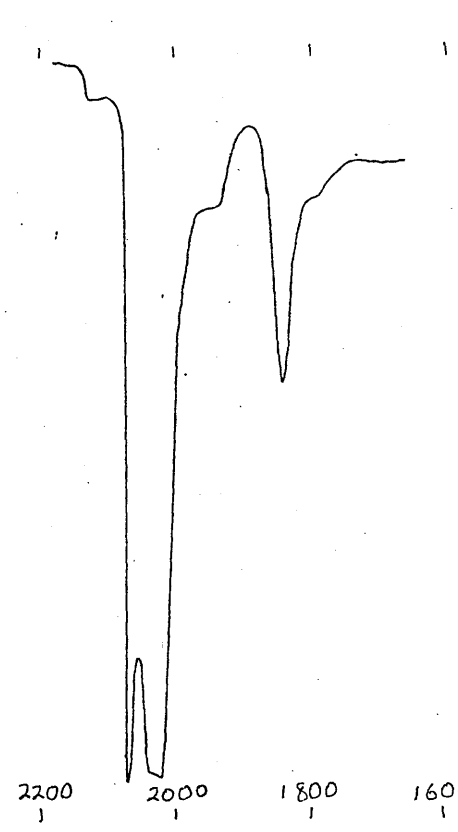
after 10mins

Figure 2.37



a) after 20hrs b) after 24hrs

Figure 2.38



$Co_2(CO)_8$ in tolune

Figure 2.39

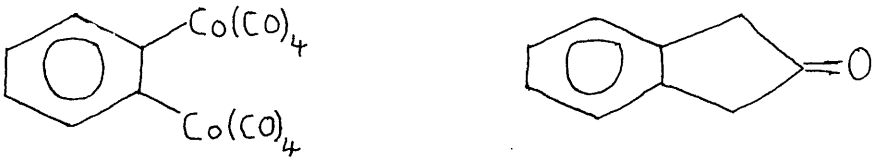
$Co_4(CO)_{12}$ remained after twenty four hours (Fig. 2.38b).

The results described in this section are summarised in Table. 2.5.

Two other ethereal solvents were used - ethyleneglycol dimethyl ether (glyme) and diethyleneglycol dimethyl ether (diglyme). Both paralleled T.H.F. in that under carbon monoxide the solvent alone would disproportionate $Co_2(CO)_8$ to $[Co(CO)_4]^-$ and addition of LiBr reduced the reaction time to five minutes, LiI to ten minutes. Both cause disproportionation of $Co_2(CO)_8$ faster than T.H.F. itself.

4. DISPROPORTIONATION IN HYDROCARBON SOLVENTS.

The only hydrocarbon solvent studied was toluene. Twenty hours of $Co_2(CO)_8$ residing in this solvent showed no more difference (spectroscopically) than after five minutes (Fig. 2.39). Addition of various reagents did not induce reaction either, e.g. LiBr (twenty four hours) NaBr (seventy two hours), Ph_4PBr (forty hours), $CoBr_2$ (fourteen hours under nitrogen) $LiBH_4$ and $LiBF_4$ (both twenty four hours) and $LiPF_6$ (seventy hours). For the reaction of $Co_2(CO)_8$ and NaBr, some α,α'- dibromo - o-xylene was added. This will react with any anion present to form the intermediate of Fig. 2.40a which in turn forms 2-indanone[182] (Fig. 2.40b). This showed no reaction after twenty four hours.



(a) (b)

Figure 2.40

Reaction of $Co_2(CO)_8$ with Various Catalysts in Diethyl Ether, after 24 Hours.

Catalyst	Products formed under Nitrogen	Products formed under Carbon Monoxide
LiBr	$Co_4(CO)_{12}$	$[Co_3(CO)_{10}]^-$ + $[Co(CO)_4]^-$ + $Co_2(CO)_8$
NaBr	$Co_4(CO)_{12}$	$[Co_3(CO)_{10}]^-$ + $[Co(CO)_4]^-$ + $Co_2(CO)_8$
Bu_4NBr	$Co_4(CO)_{12}$ + $Co_2(CO)_8$	$[Co(CO)_4]^-$ + $Co_2(CO)_8$
Ph_4PBr	N/A	slight loss of $Co_2(CO)_8$; no other species present
$LiBH_4$	N/A	$[Co_3(CO)_{10}]^-$(?) + $[Co(CO)_4]^-$ + $Co_2(CO)_8$
$LiBF_4$	N/A	no reaction
$LiPF_6$	$Co_4(CO)_{12}$	$Co_2(CO)_8$ + traces of $Co_4(CO)_{12}$
LiOH	N/A	no reaction
$CoBr_2$	$Co_4(CO)_{12}$	$[Co_3(CO)_{10}]^-$(?) + $Co_2(CO)_8$

N/A Not Available.

Table 2.5.

5. EXPERIMENTAL

a) Purification of Reagents and Solvents.

$Co_2(CO)_8$ was used as supplied by the manufacturers without further purification. The material is unstable and so was kept at -5^oC under nitrogen or argon when not in use. Exposure to air was minimal, during weighings, with the weighing bottles being flushed with nitrogen before use. $Co_2(CO)_8$ was allowed to reach room temperature before being handled. Reactions involving $Co_2(CO)_8$ were always conducted in an atmosphere of nitrogen or carbon monoxide.

The halide salts and lithium salts, except $LiBF_4$ and $LiBH_4$ were used as provided; the only precaution taken was to heat them at 100^oC in vacuo overnight to remove traces of water (lithium salts are especially hygroscopic). Because $LiBF_4$ and $LiBH_4$ will decompose under such conditions (losing BX_3, X = H or F) these were used as supplied with the minimum possible exposure to air.

Toluene was dried over sodium wire before use; otherwise no further purification was thought necessary.

Diglyme and glyme were distilled, under nitrogen, and stored over activated molecular sieves in an inert atmosphere (both react with sodium wire to give a brown sludge).

Diethyl ether was dried roughly using sodium wire then distilled, from magnesium sulphate ($MgSO_4$) and stored, under nitrogen, over activated molecular sieves. More usually it was distilled when necessary directly into the reaction vessel to avoid absorption of water (because of ether's ability to "creep", it is difficult to make its container air-tight and thus moisture free).

T.H.F. having a great affinity for water was purified and stored in a semi-permanent set-up. After checking that it was peroxide free (by iodine - starch indicator paper), it was roughly dried using sodium

wire, then distilled under nitrogen into a large three necked round bottomed flask (commonly one litre in capacity). Fresh sodium wire (added directly from the sodium press) and benzophenone were added under a nitrogen stream and the vessel sealed. Periodically over the next twenty four - forty eight hours the flask was shaken, with more sodium wire and/or benzophenone added as required. When the solution remained deep blue in colour it was deemed to be dry. The intense colour is brought about by the formation of sodium benzophenone ketyl which is immediately decomposed by water. Although an old method of drying, it is very efficient[227]. When T.H.F. was required for use it was distilled, under nitrogen, from this stock solution directly into the reaction vessel. Warning : add the sodium wire and benzophenone over a period of time. If in an attempt to dry the solvent quickly, too much of either is added, the result is a deep blue gel which should be disposed of. For one litre at least one fair sized chunk of sodium and a few grams of benzophenone are necessary.

b) General Procedures.

When drying ethereal solvents, by distillation, an atmosphere of nitrogen should be always used to eliminate the formation (and potential explosion) of peroxides. For the same reason a rapid turnover of solvents was employed, with the last fraction of each batch including the drying reagent always being discarded (care is needed since some active sodium wire is still likely present; 2-propanol is recommended for destroying the sodium, followed by small amounts of water).

As mentioned the gases used as experimental atmospheres were nitrogen (supplied as oxygen free), and carbon monoxide. To ensure they were both oxygen and moisture free they were made to pass through an elaborate drying tray, outlined in Fig. 2.41. The purpose of the nujol bubblers on the inlet side was to avoid suck-back in either direction if any build up

EXPERIMENTAL APPARATUS

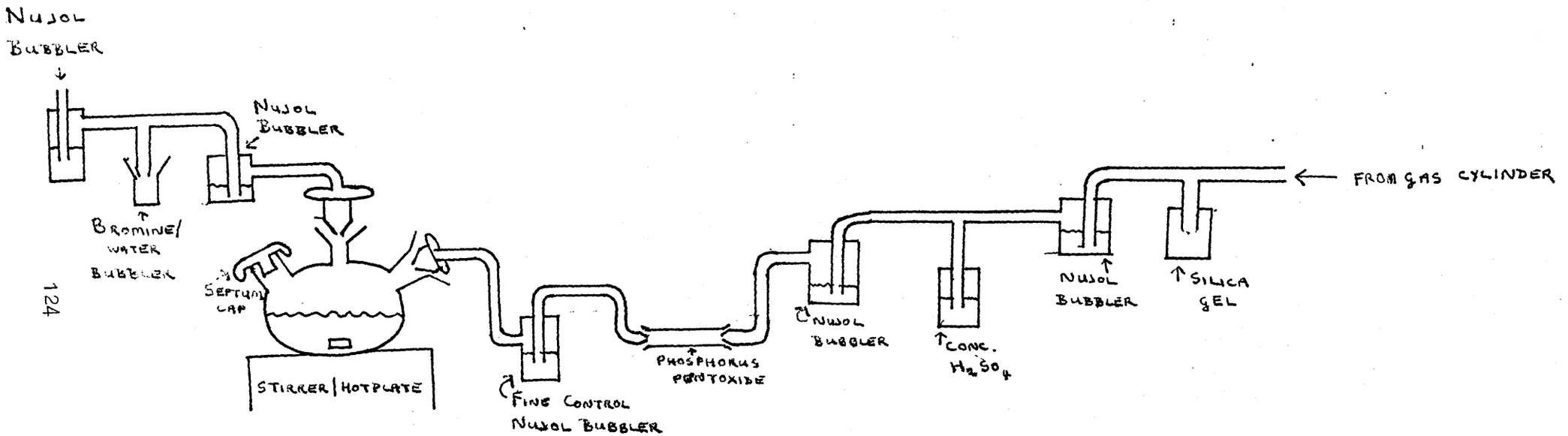


Figure 2.41

of pressure occurred. The line was renewed frequently when necessary. On the outlet side of the reaction vessel any gaseous products (including carbon monoxide or nitrogen) were made to pass through an assortment of bubblers. The nujol bubblers are again to avoid suck-back or air contamination while the bromine - water bubbler is to destroy any obnoxious byproducts, the most likely being $HCo(CO)_4$.

For the main part the reaction vessel itself was a simple 100 ml, 3 necked round bottomed flask fitted with two stopcock adaptors (to serve as gas inlets and outlets) and a septum cap (to enable samples to be added or withdrawn by syringe). All glassware was baked out in an oven before use and assembled while still hot. The joints were greased with silicone or apiezon L grease. The reaction vessel was then purged with the atmosphere of choice (while cooling to room temperature) and the solvent added/distilled in. Solid reagents were added against a strong counter-current of gas while liquid reagents were added by syringe. To stir solutions the flasks were equipped with a magnetic stirrer bar operated by a stirrer/hotplate.

Any experiments being left overnight had the septum cap replaced by a greased stopper, all joints being sealed using parafilm tape before the gas flow was shut off. After the experiments were finished, all cobalt containing materials (solution or solid) to be disposed of, were destroyed using ethanol.

All reactions, including the distillation of solvents, were conducted in a spark free fume hood.

c) Spectroscopic Techniques

Aliquots of the reaction solutions were withdrawn by syringe under a positive gas flow and injected directly into the i.r. cell. The cell used was the RIIC FH-01 fitted with synthetic sapphire windows and drilled to take a needle. The pathlength throughout was 0.1 mm.

A matching cell containing the solvent of the experiment was placed in the reference beam of the spectrometer, thus eliminating any solvent absorption. The cells were held in RIIC VLT-2 variable temperature cell holders. For work at $0^{o}C$ these were cooled by packing ice in their central column.

For solution i.r. the Perkin Elmer 577 initially then the Perkin Elmer 337 and 257 spectrometers were used; the former scans at 200 cm^{-1} per minute below 2000 cm^{-1}, and 400 cm^{-1} per minute above 2000 cm^{-1}, the 337 scans at approximately 375 cm^{-1} per minute on Range I (i.e. the grating change is above 2100 cm^{-1}) and the latter spectrometer scans at 400 cm^{-1} per minute on Range I. Routinely the region between 2300 and 1600 cm^{-1} was recorded. Solid samples had their i.r. spectrum recorded on the Perkin Elmer 580 spectrometer in K.Br disc form.

Sapphire windows were used to eliminate the possible interaction of halide windows with the solutions[228] (especially since in most reactions being studied this would lead to an artificially high rate of disproportionation). They are also easier to handle, for cleaning purposes, and can be used for water containing solutions. The major drawback is that sapphire absorbs below 1500 cm^{-1}, cutting off any further spectral information. As this work was concerned with metal carbonyl stretches above 1700 cm^{-1}, this happily presented no such problem.

The method of filling the solution cell via a syringe was found to be adequate, there being no appreciable deterioration in the solution (due to, e.g., air oxidation). More elaborate techniques involving connection of the i.r. cell directly with the reaction vessel have been employed[165] but not thought necessary here.

After recording the i.r. spectrum the sample cell was emptied and rinsed out with the solvent in current usage (or by ethanol followed by the solvent) before being reloaded. The first fraction of any

aliquot was syringed through the cell removing any air, solvent etc., before the cell was filled.

N.B. All reaction times quoted refer to time elapsed since the reaction was initiated until the spectrometer started to record the spectrum. In general the practices outlined were adhered to throughout the course of recording i.r. spectra unless otherwise indicated in the text. In this chapter the spectrometer used was the Perkin Elmer 337, unless otherwise stated.

For visible/ultra violet spectroscopy, the spectra of the solids were recorded using their KBr disc form (from their solid i.r. spectra) on the Pye - Unicom SP8 - 100 spectrometer with a pure KBr disc in the reference beam. Solution visible / ultra violet spectra were recorded on the Beckman 5270 spectrometer, unless otherwise noted.

d) The Experiments

(1) $Co_2(CO)_8$ in Varying Solvents.

The reaction vessel illustrated in Fig. 2.41 had roughly 50 ml T.H.F. or diethyl ether distilled in, under nitrogen, then purged with the atmosphere of the experiment. For experiments using diglyme, glyme or toluene, 50 ml dried solvent was added directly, against a counter-current of the required gas. 0.513 g solid $Co_2(CO)_8$ [1.50×10^{-3} moles] was added, again against a counter - current of gas, while stirring. The progress of the reaction was followed by withdrawing samples of the solution at regular intervals. The solutions were dark brown at the onset of the reaction, with production of anion tending to lighten the colour. Solutions containing only $[Co(CO)_4]^-$ and Co^{2+} were dark green in hue. The reactions were monitored over various lengths of time (hours or days) depending on the rate of reaction.

(2) Valence Disproportionation of $Co_2(CO)_8$ by Lithium Halides in T.H.F., Glyme and Diglyme.

To 50 ml solvent, 0.513g $Co_2(CO)_8$ [1.50×10^{-3} moles] was added against

the appropriate gas flow. An i.r. spectrum of the solution was obtained (to check the condition of $Co_2(CO)_8$ and to give an initial concentration at t_o) and then approximately 0.17g LiBr [1.96×10^{-3} moles] or 0.27g LiI [2.02×10^{-3} moles] was added.

The previously dark brown solution immediately showed evidence of gas evolution and within five minutes the solution was the characteristic dark green of the anion containing solution ready for further experiments. An i.r. spectrum confirmed $[Co(CO)_4]^-$ as being the only cobalt carbonyl containing species in solution.

(3) Reactions with $Co_2(CO)_8$ by Other Lithium Salts.

The basic procedure outlined about in part (2) was followed. For $LiBH_4$ containing experiments about 0.062g [2.85×10^{-3} moles] was added to the different solutions of $Co_2(CO)_8$ under a carbon monoxide atmosphere. There was an immediate gas evolution (c.f. LiBr case) when T.H.F. was used with the solution becoming lighter in colour, the white $LiBH_4$ taking about half an hour to totally dissolve. Using diethyl ether, gas evolution coincided with a red / blackcurrant colour. (This can be compared with experiments involving $[Co_3(CO)_{10}]^-$ of chapter 3). $LiBH_4$ in toluene solutions would not dissolve, let alone react.

For all $LiBH_4$ experiments (and $LiBF_4$ experiments), an acetone bubbler was placed between the reaction vessel and the first nujol bubbler on the outlet side to destroy any BH_3 (or BF_3) formed during reaction. When $LiBF_4$ was used, the amounts added were in the region of 0.21g [2.24×10^{-3} moles] under a carbon monoxide atmosphere. In T.H.F., diethyl ether and toluene a dark brown solution persisted, any reaction (in the first two solvents) being a result of solvent attack on $Co_2(CO)_8$. For $LiPF_6$ about 0.31g [2.04×10^{-3} moles] was used. In experiments under carbon monoxide the reagent took an hour to completely dissolve leaving a dark brown solution. Similar observations as for $LiBF_4$ experiments were made.

Under nitrogen and in diethyl ether $Co_4(CO)_{12}$ was eventually formed with $[Co(CO)_4]^-$ and $[Co_3(CO)_{10}]^-$ being present along with $Co_2(CO)_8$ in the intervening stages. In T.H.F. a steady mixture of $Co_4(CO)_{12}$, $[Co_3(CO)_{10}]^-$ and $[Co(CO)_4]^-$ is established which persists for several days.

0.226g $Co_2(CO)_8$ [6.61×10^{-4} moles] and 0.025g LiOH [1.04×10^{-3} moles] were added to diethyl ether but LiOH did not display any tendancy to dissolve or to react with $Co_2(CO)_8$.

(4) Valence Disproportionation of $Co_2(CO)_8$ by Other Halide Salts.

The basic procedure of part (2) is again followed, using carbon monoxide as an atmosphere unless otherwise stated.

For experiments involving NaBr, 0.21g [2.04×10^{-3} moles] of the reagent was used with 0.513g $Co_2(CO)_8$ [1.50×10^{-3} moles]. In T.H.F. the observations matched those of the LiBr reaction i.e. gas evolution (carbon monoxide) and the colour of solution becoming dark green as time passed. For the complicated mixture of species obtained in diethyl ether, the dark brown colour persisted. No reaction was visible in toluene.

Under nitrogen, NaBr in diethyl ether reacted with $Co_2(CO)_8$ to give $Co_4(CO)_{12}$ (a dark brown solution) with some white solid (undissolved NaBr ?). In T.H.F., the solution was dark green after half an hour, although $[Co(CO)_4]^-$ did not dominate the i.r. spectrum for a further half an hour and was not the sole product until two hours had elapsed since the start of the reaction.

Between 0.64 and 0.65g n-Bu_4NBr [2.0×10^{-3} moles] was required to react with 0.513g $Co_2(CO)_8$ [1.50×10^{-3} moles], according to the equation:

$$3Co_2(CO)_8 + 4X^- \longrightarrow 4[Co(CO)_4]^- + 2CoX_2 + 8CO \qquad (2.33)$$

Addition of the reagent, in T.H.F., led to rapid gas evolution and a dark green solution after five minutes. At this stage $[Co(CO)_4]^-$ dominates the i.r. spectrum but a further hour is required to lose the last traces of $Co_2(CO)_8$. In diethyl ether the solution gradually lightened in colour, until it was pale green, as the anion concentration built up over one to two hours. When nitrogen was used slow formation of $Co_4(CO)_{12}$ was noted.

0.67g $n\text{-}Bu_4PBr$ [1.97×10^{-3} moles] was added to a standard strength solution of $Co_2(CO)_8$ in T.H.F., leading to gas evolution and a dark green solution. Again only traces of $Co_2(CO)_8$ was in evidence after five minutes and these had vanished within the hour.

Approximately 0.84g Ph_4PBr [2.00×10^{-3} moles] when added to $Co_2(CO)_8$ in T.H.F. led to some gas being evolved but the solution remained dark brown with a white precipitate initially (Ph_4PBr). After ten minutes had elapsed the solution was dark green with a little white solid and after thirty minutes only $[Co(CO)_4]^-$ remained. In diethyl ether the initial i.r. spectrum of the mixture of $Co_2(CO)_8$ and Ph_4PBr resembled that of $Co_2(CO)_8$ in THF, not ether. Gradual loss of the i.r. signals is observed over a period of days with a green crystalline material appearing (first noticed after one hour of reaction).

For experiments involving $CoBr_2$ the solid was not used until it was bright green in colour (any traces of moisture will result in a purple colouration). A large excess of $CoBr_2$ (about 1.5g [6.86×10^{-3} moles]) was added in turn to toluene, T.H.F. and diethyl ether solutions of $Co_2(CO)_8$ under carbon monoxide. As expected no effect whatsoever was noted with toluene, $CoBr_2$ disdaining to dissolve. In T.H.F. conversion to 50% anion took 48 hours, as a result of solvent activity. In diethyl ether, a modification of the terminal carbonyl region is found after twenty hours - production of $Co_4(CO)_{12}$ is suspected. The solution was

olive green / brown initially, mainly because of the strong colouration of $CoBr_2$, but was brown after ten minutes. In the other reactions involving $CoBr_2$ a dark brown colour persisted throughout.

Under nitrogen and in toluene $CoBr_2$ failed to dissolve and so no reaction was observed. In T.H.F., 4 ml of a blue concentrated T.H.F. solution of $CoBr_2$ was injected into the $Co_2(CO)_8$ solution, resulting in a gas being evolved and the mixture becoming green in colour. Anion production was observed, by i.r., in conjunction with the growth of a signal at 1960 cm^{-1} which is thought to be due to a $Co_2(CO)_7$ (T.H.F.) type species. Support for this assignment was forthcoming when a change of atmosphere to carbon monoxide reversed the reaction, with traces of $Co_2(CO)_8$ being in evidence after one hour; after three hours only $Co_2(CO)_8$ and $[Co(CO)_4]^-$ were present in solution at an equilibrium which was stable for several days. The solution also changed to a green / brown colour.

(5) Preparation of $Fe(o\text{phen})_3Cl_2$.

After a search of the literature, the only simple preparation of iron phenanthroline salts found was for the preparation of $Fe(o\text{phen})_3\ SO_4$[229a]. This method was adapted, using $FeCl_2$ instead of $FeSO_4$ and is outlined below.

A 1:3 ratio of $FeCl_2.\ xH_2O$: ophenanthroline.H_2O is dissolved in water to give $Fe(o\text{phen})_3Cl_2$ in aqueous solution.

e.g. to make a 0.025M solution in 25 ml water, 0.1244g ferrous chloride tetrahydrate ($FeCl_24H_2O$) [6.25×10^{-4} moles] plus 0.3719g ophenanthroline monohydrate ($C_{12}H_9N_2H_2O$) [1.87×10^{-3} moles] were used. The ferrous chloride was dissolved in approximately 20 ml water with a little of this water used to rinse out the weighing bottle, the washings being added to the flask. This gave a green / yellow solution on gentle heating. When it was completely dissolved, the white ophenanthroline

powder was added resulting in an immediate spectacular change of colour to blood red. Further gentle heating was necessary to complete the dissolution of ophenanthroline, then the solution was allowed to regain room temperature. Transfer of the solution to a graduated flask, complete with the washings of the reaction flask, followed and the solution was made up to the mark with the remainder of the water (Deionised water was used throughout). I.r. analysis of the solid (obtained by evaporation of the solvent) was obtained (Fig. 2.42).
To make the nickel derivative, nickel chloride hexahydrate ($NiCl_2 6H_2O$) [0.1486g, 6.25×10^{-4} moles] replaced the corresponding iron compound. Otherwise the method is the same.

(6) Preparation of $Co(BF_4)_2$ T.H.F.$_x$

The main problem in such preparations is to eliminate water from the reactions. The common method to prepare transition metal tetrafluoroborate compounds is to react the appropriate anhydrous silver salt with excess metal halide or use stoichiometric amounts of each salt where the halide is soluble[229b]. For cobalt bis tetrafluoroborate, $Co(BF_4)_2$, in diethyl ether, a blue precipitate is formed but it is difficult to get the reaction to go to completion because of formation of the intermediate halide salt $Co(BF_4)Cl$. No matter what methods of drying were employed e.g. thermal decomposition, pumping over phophorus pentoxide, heating in vacuo, water could not be totally removed from the product, or intermediate; on the odd occasion that it was possible, decomposition of the salt resulted - this applied to all first row transition metals. After a great deal of thought, the simplest method of obtaining the salt was by metathesis using silvertetrafluoroborate, $AgBF_4$, as the starting point. As this compound cannot be purified once the monohydrate is formed, great care was needed to keep the salt dry. It had been shown that $Co(BF_4)_2$ or $Co(BF_4)X$ (X = halide) salts were stable when

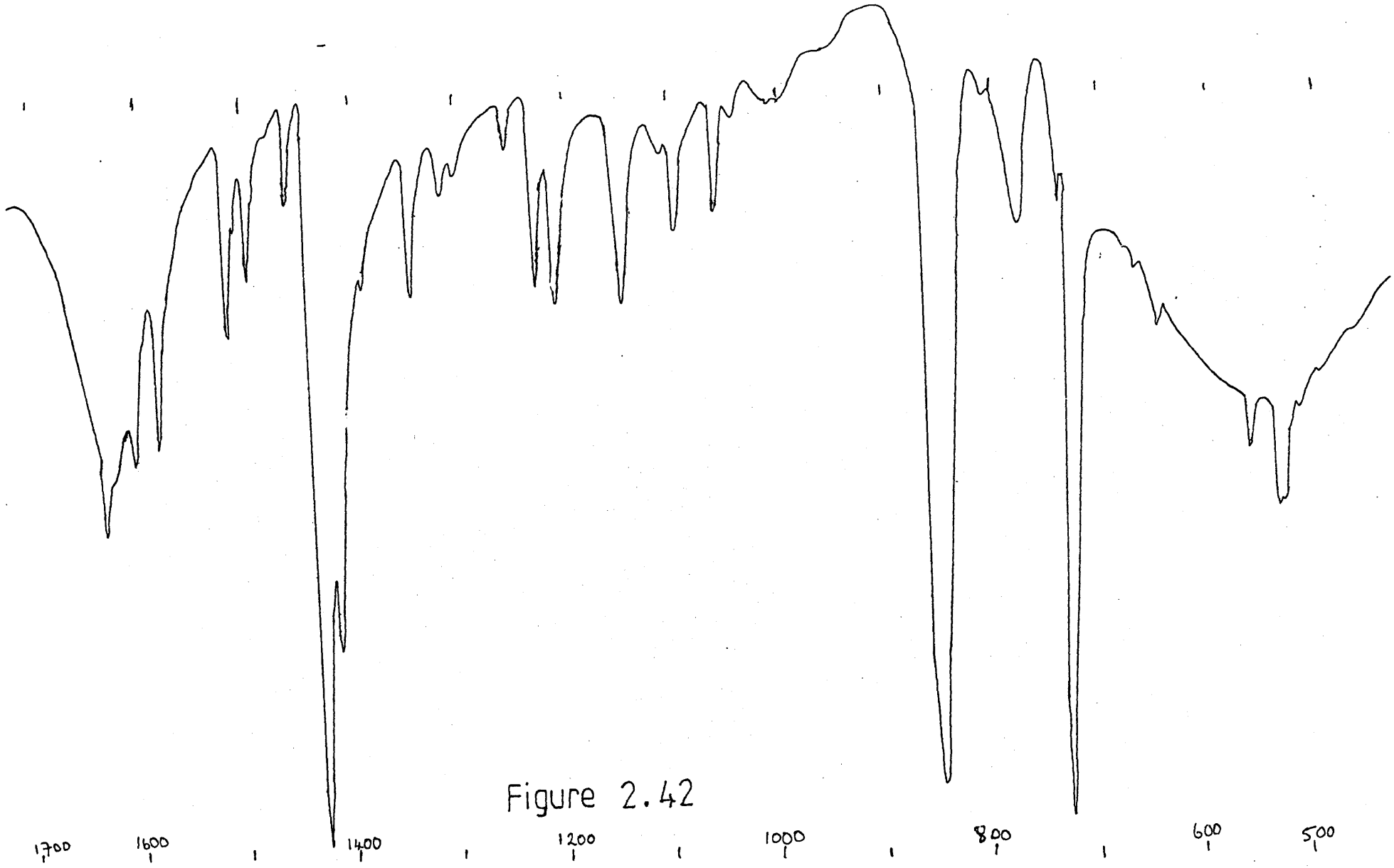


Figure 2.42

the Co^{2+} ion is fully coordinated[229c] and so the reaction was carried out in T.H.F. which would coordinate to Co^{2+}, with no attempt being made to isolate the salt.

$AgBF_4$ was placed in a rotoflow vessel, wrapped in aluminium foil, with a side arm, under nitrogen. The role of the foil was to eliminate light from the light sensitive compound. The vessel was then pumped down in vacuo. Anhydrous $CoBr_2$ was placed in a round bottomed flask and heated in vacuo for two hours to remove any remaining traces of moisture. The apparatus for this, and the rest of the experiment, is shown in Fig. 2.43.

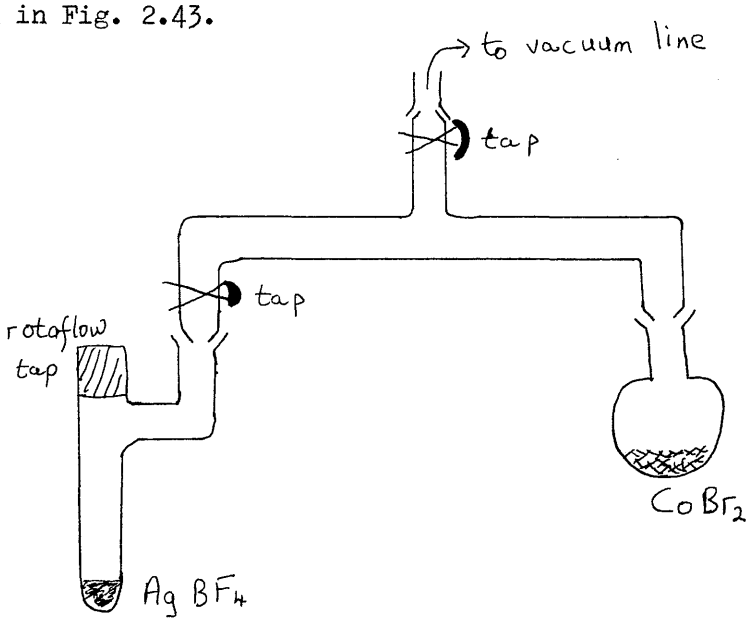


Figure 2.43

50 ml anhydrous T.H.F. was distilled into the flask containing $CoBr_2$ and shaken until all the green solid had dissolved. This solution was decanted into the rotoflow vessel containing the silver salt, a nitrogen atmosphere introduced, then shaken for six hours to give a whitish precipitate, silver bromide, and a blue solution. This was filtered under nitrogen into a round bottomed flask and stored, ready for use. A i.r. spectrum of the solution showed no traces of water.

To eliminate the problems of water absorption by silver salts, the preparation of cobalt bis hexafluorophosphate, $Co(PF_6)_2$, was attempted

using $CoBr_2$ and nitrous hexafluorophosphate, $NOPF_6$. This was not possible since $NOPF_6$ reacts with T.H.F., polymerising it.

(7) Reaction of $Co_2(CO)_8$ with $Co(BF_4)_2$ T.H.F.$_x$.

0.251g $Co_2(CO)_8$ [7.34×10^{-4} moles] was placed in a 100 ml, 3 necked round bottomed flask containing 50 ml freshly distilled T.H.F., under carbon monoxide, to give a dark brown solution. This was the blank experiment. Into an identical flask containing 80 ml of solvent and under carbon monoxide 3 ml $Co(BF_4)_2$ T.H.F.$_x$ was syringed to give a light blue solution. Addition of 0.250g $Co_2(CO)_8$ [7.31×10^{-4} moles] gave an olive green / brown solution (because of the mixture of colours, not reagents). A slight lightening of colour was the only change with time. Under nitrogen, the solution slightly darkened in colour, becoming a darker brown. The thin film i.r. spectrum (run on the P.E.580) and the visible / U.V. spectrum are shown in Fig. 2.44.

(8) Reaction of $[Co(CO)_4]^-$ with $Co(BF_4)_2$ T.H.F.$_x$.

0.764g $Ph_4PCo(CO)_4$ [1.50×10^{-3} moles] was added to 50 ml freshly distilled T.H.F. under a carbon monoxide atmosphere to give a green solution, and an i.r. spectrum as expected of $[Co(CO)_4]^-$. Addition of 3 ml $Co(BF_4)_2$ T.H.F.$_x$ followed, making the solution a darker apple green colour. The i.r. spectra recorded over the next 60 hours showed no change whatsover, whether under carbon monoxide, or later, under nitrogen. The colour of solution did not alter either.

(9) Isolation of $[Co(CO)_4]^-$ Salts.

After producing purely anionic species under certain reaction conditions, attempts were made to isolate the species as an ionic solid. Addition of 20 ml 0.025M aqueous $Fe(o\text{phen})_3Cl_2$ to a solution conatining $[Co(CO)_4]^-$ prepared from $Co_2(CO)_8$ and $LiBH_4$ in T.H.F. under carbon monoxide, resulted in a red solid being precipitated from solution after one hour of stirring. The solution was transferred to a flask with a further 20 ml deionised

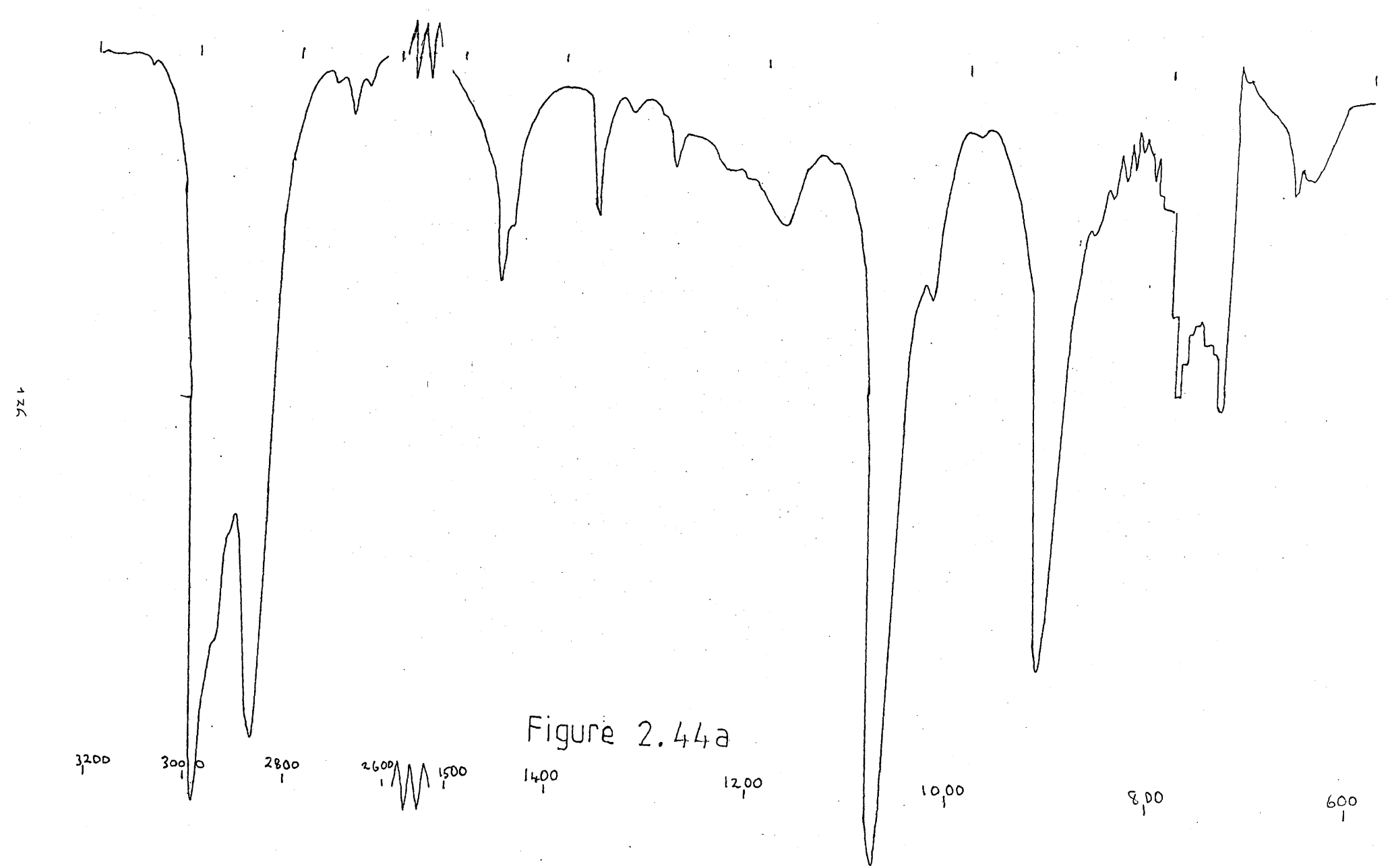


Figure 2.44a

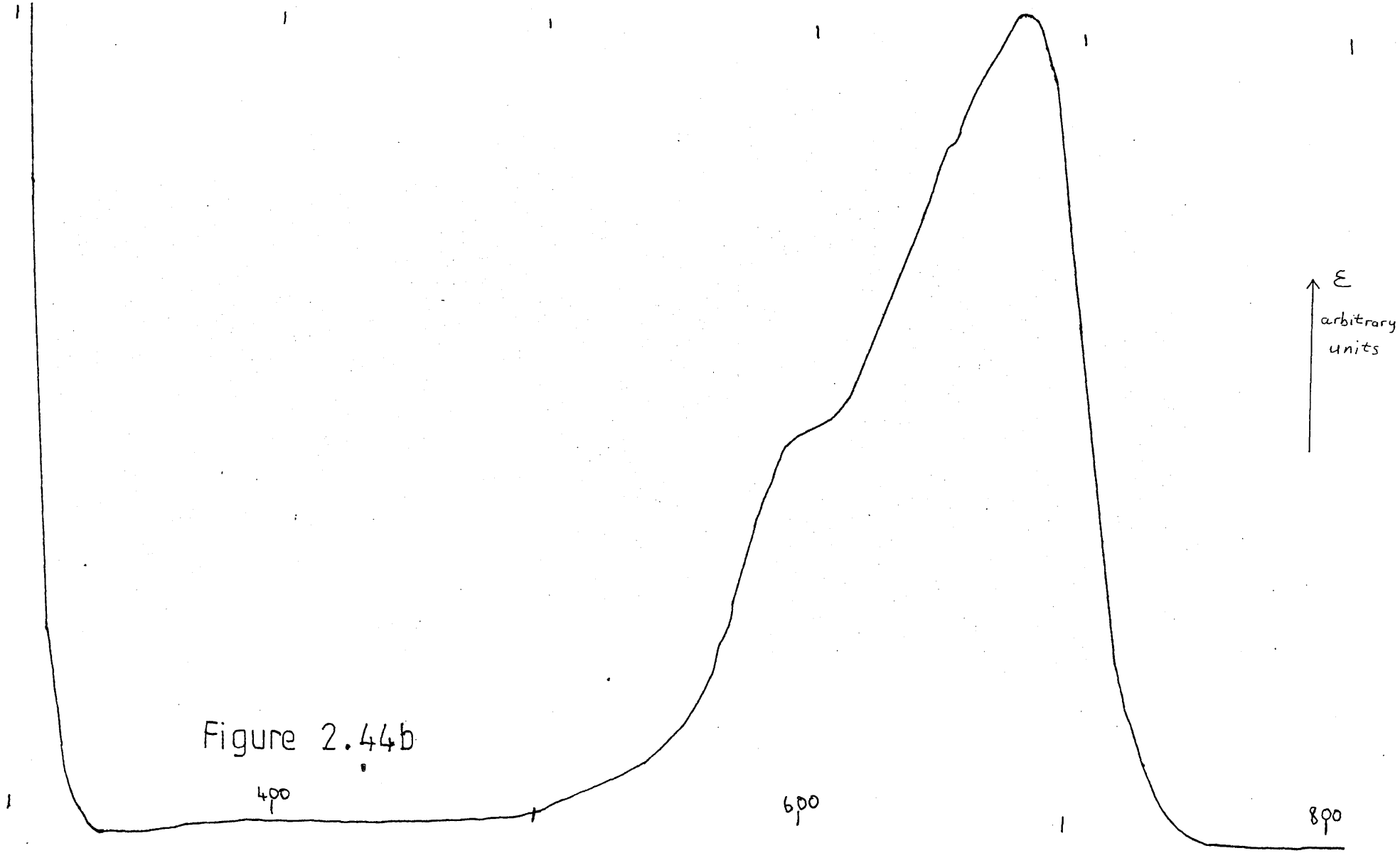


Figure 2.44b

water and allowed to stand. Filtration at the water pump followed, yielding a red solid.

For the reaction of n-Bu_4NBr with $Co_2(CO)_8$ in T.H.F., the product $[n\text{-}Bu_4N]^+[Co(CO)_4]^-$ was isolated. This involved transferring the green solution from the reaction vessel, under carbon monoxide, to a larger flask and adding 500 ml deionised water to precipitate the compound, known to be insoluble in water[202]. However this method resulted in decomposition of the compound during separation and so an alternative method was employed. First the solvent , that is T.H.F., was removed by rotoevaporation leaving a peacock blue solid comprising the product and $CoBr_2$. Addition of 100 ml water gave a green / white solid plus a clear solution. 5 ml dilute hydrochloric acid then gave a green solid and pink solution (due to $[Co(H_2O)_6]^{2+}$). Separation gave the solid product whose i.r. spectrum confirmed it to be n-$Bu_4NCo(CO)_4$ - see Fig. 2.45. This compound is unstable in air decomposing to a black mass. n-$Bu_4PCo(CO)_4$ was isolated in the same manner, the solid proving more yellow / green in hue.

Obtaining $Ph_4PCo(CO)_4$ from diethyl ether solutions was much simpler. As it is insoluble in this solvent, the pale green solid can be collected by filtration of the reaction mixture. In T.H.F. where it is soluble, the procedure outlined for n-$Bu_4NCo(CO)_4$ salts is employed. If T.H.F. is not removed before the addition of water, the amount of water required is increased five or six-fold. Since this gives a larger timescale for the filtration step, decomposition is likely. The main reason for using water at this stage is because the byproducts of Co^{2+} salts are soluble whereas the desired product is completely insoluble.

(10) Reaction of $Co_2(CO)_8$ / LiX with Allyl Bromide.

This reaction was carried out using diethyl ether solutions prepared by the action of LiX (X = Br, Cl) on $Co_2(CO)_8$, under nitrogen, as previously

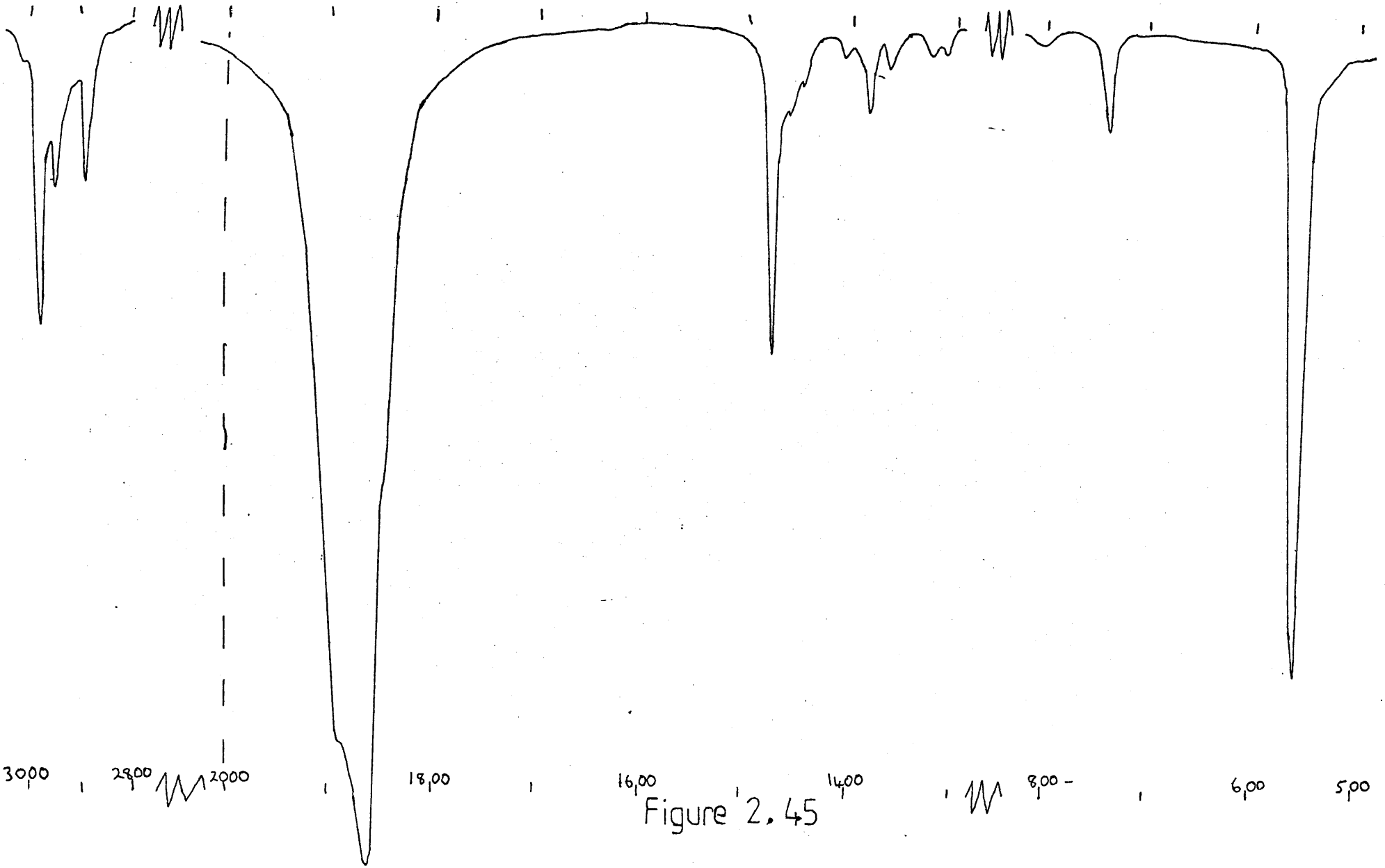


Figure 2.45

described. After two hours, 170 μl allyl bromide [1.96 x 10^{-3} moles] was added, and within half an hour evidence of the end product was furnished by the i.r. spectrum, the reddish / brown solution having become dark green in colour. Reaction was complete within another hour to give a light green colour and so 0.53g Ph_3P [2.02 x 10^{-3} moles] was added giving a 1:1 ratio of Ph_3P: $[Co(CO)_4]^-$. Within ten minutes an olive green solution was observed which had an i.r. spectrum characteristic of $\langle$—— $Co(CO)_2(Ph_3P)$. The solution lightened in colour with a dark green / brown solid also present.

A similar experiment, under nitrogen, was conducted but this time addition of allyl bromide preceeded that of LiX. 170 μl allyl bromide [1.96 x 10^{-3} moles], 0.513g $Co_2(CO)_8$ [1.50 x 10^{-3} moles] in 50 ml diethyl ether gave a dark brown solution, but no reaction after one hour. 0.13g LiI [9.71 x 10^{-4} moles, half of the stoichiometric amount] was added and within fifteen minutes, i.r. absorptions of the dark green solution, corresponding to $\langle$—— $Co(CO)_3$, along with $Co_2(CO)_8$ were noted, but no $[Co(CO)_4]^-$ bands. The remaining 0.13g LiI resulted in the reaction going to completion with the solution becoming light green. 0.53g Ph_3P [2.02 x 10^{-3} moles] when added changed the colour to olive green immediately and the i.r. spectrum revealed the final product after ten minutes. As before the final solution was pale green with a brown / green precipitate present.

Using 0.74g n-Bu_4NBr [2.30 x 10^{-3} moles] instead of LiX as the catalyst gave similar results.

(11) <u>Reaction of $[Co(CO)_4]^-$ with with methyl iodide</u>.

A solution of $Ph_4PCo(CO)_4$ in T.H.F. was prepared, under nitrogen, by the reaction of 0.513g $Co_2(CO)_8$ [1.50 x 10^{-3} moles] with 0.84g Ph_4PBr [2.00 x 10^{-3} moles], as previously described. The reaction was cooled to 0°C using an ice bath and the i.r. cell holders were then cooled in a similar manner. 0.38 ml methyl iodide [6.10 x 10^{-3} moles] which

is an excess amount, was added by syringe resulting in the dark brown / green solution lightening, becoming dark green over the next two and a half hours. This is because of the slow consumption of the anion to give the alkyl cobalt carbonyl species, $MeCo(CO)_4$. The solution was left at 0^oC overnight, remaining green in colour. On warming up to room temperature acetone was formed, its presence being indicated by an i.r. absorption at 1720 cm^{-1}. There was no obvious change in the colour.

6. DISCUSSION

In toluene no reaction is noted with any of the reagents tested, either under carbon monoxide or under nitrogen. The discussion below will be restricted to ethereal solvents.

The first contrast to be noted is in the different effects of $[CoX_4]^{2-}$ (as the potassium salt) and CoX_2 (X = Br, Cl) on solutions of $Co_2(CO)_8$ in T.H.F. The former reagent is used in valence disproportionation with great success[182], while the latter has barely any effect. This can be rationalised by comparing the tightness of bonding between the cobalt and the halide in each complex. In $[CoX_4]^{2-}$ there is a greater negative charge on each halide and weaker cobalt - halide bonding than in CoX_2. This enables the halide to be freer and so it can attack the $Co_2(CO)_8$ molecule with greater gusto, causing disproportionation i.e. it is free, or nearly free, halide that is responsible for disproportionation, not a cation or a neutral species.

The appearence of the i.r. absorption at 1940 cm^{-1} when $CoBr_2$ and $Co_2(CO)_8$ are reacted in T.H.F. under nitrogen has been tentatively assigned to $Co_2(CO)_7$(T.H.F.) where T.H.F. has replaced a terminal carbonyl group. No record of this species could be found in the literature although $Co_2(CO)_7(Ph_3P)$ has been made and described[230] ($\bar{\nu}$ (CO): 2079w, 2026m, 2010sh, 1996s, 1964m cm^{-1} indicating a C_{3v} structure). A

similar mystery species was found in the reaction of $^{t}AmONa/Co_2(CO)_8$ or $NaH/^{t}AmONa/Co_2(CO)_8$ in T.H.F. under carbon monoxide; there the i.r. bands were 1955 and 1940 cm^{-1} which disappeared on heating the solution for two hours at 63°C[168]. A suggested mechanism is outlined in Fig. 2.46.

$$Co_2(CO)_8 + CoBr_2 \xrightarrow{N_2} Co_4(CO)_{12} + \text{negative cobalt carbonyl clusters} + [Co(CO)_4]^-$$

$$\downarrow CO \qquad\qquad \downarrow CO$$

$$Co_2(CO)_8 + \text{cluster compounds} + [Co(CO)_4]^- \qquad Co_2(CO)_8 + [Co(CO)_4]^-$$

Figure 2.46

In general the disproportionation of $Co_2(CO)_8$ in T.H.F., under carbon monoxide, is straightforward when the catalyst is in the form RX, where R is an alkali metal or large organic hydrocarbon cation and X is the halide ion. Similar, easy to explain reactions occur in diglyme and glyme. Perhaps it would be more accurate to say that the halide salt is a reagent, not a catalyst, since it is not regenerated and in some experiments is actively removed from the reaction solution.

In ether the reaction is slower and produces more than one ionic species. This can be rationalised by saying that the disproportionation of $Co_2(CO)_8$ can give $[Co_3(CO)_{10}]^-$ or $[Co(CO)_4]^-$ or a mixture of both. $[Co_3(CO)_{10}]^-$ is by far the less stable of the two and so in T.H.F., where the lithium ion is coordinated by solvent molecules, this anion is rarely seen and so mainly $[Co(CO)_4]^-$ is observed. In diethyl ether the poorer donor solvent, Li^+ is relatively uncoordinated and so can stabilise $[Co_3(CO)_{10}]^-$ to such an extent that it can co-exist with $[Co(CO)_4]^-$. Why this carbonyl deficient species, with a Co:CO ratio of $1:3\frac{1}{3}$ is present in a carbon monoxide environment at all (both $Co_2(CO)_8$ and $[Co(CO)_4]^-$ have a Co:CO ratio of 1:4) is not fully understood; it is presumed that this is an equilibrium effect with a

complicated but finely balanced relationship between $Co_2(CO)_8$, $[Co(CO)_4]^-$, $[Co_3(CO)_{10}]^-$, Co^{2+} and free carbon monoxide. When $[Co(CO)_4]^-$ is removed from solution (e.g. by reaction with allyl bromide) this equilibrium is upset and so more $Co_2(CO)_8$ and $[Co_3(CO)_{10}]^-$ react to restore $[Co(CO)_4]^-$ to the balance. Thus total reaction can be achieved with the system ultimately behaving as if only $[Co(CO)_4]^-$ and Co^{2+} were produced from $Co_2(CO)_8$.

Using nitrogen as an atmosphere favoured formation of the carbonyl deficient species $Co_4(CO)_{12}$. Comparing this result with the mixture of $Co_2(CO)_8$ and $[Co(CO)_4]^-$ produced in T.H.F. illustrated the efficiency of the solvents w.r.t. disproportionation - in diethyl ether the rate of disproportionation is so slow that loss of carbon monoxide (to form $Co_4(CO)_{12}$ becomes the dominant pathway for decay of $Co_2(CO)_8$.

The experiments with lithium salts, with the exception of $LiBH_4$, showed that the halide is the important catalytic species, the limited reaction achieved by these compounds most likely being attributed to the solvent. The success of $LiBH_4$ in T.H.F. in emulating LiX as a disproportionation catalyst cannot solely be attributed to its solubility, lack of bulk and its Lewis acidity. Here reaction is also due to hydride attack on $Co_2(CO)_8$. In diethyl ether however the products are $Co_2(CO)_8$ and $Co_4(CO)_{12}$ with possibly some $[Co_3(CO)_{10}]^-$, the latter assignment somewhat dubious since it can only be present in small amounts and so is swamped by the absorptions of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ in the 2000 cm^{-1} region.

The experiments involving Ph_4PBr in diethyl ether indicated clearly that complexation of $[Co(CO)_4]^-$ solutions in such a solvent is not entirely due to the solvent. Although there was no i.r. evidence of $[Co(CO)_4]^-$ the simplicity of the spectrum of $Co_2(CO)_8$ resembled that of the species in T.H.F., not diethyl ether. Any $[Co(CO)_4]^-$ formed is precipitated

from solution as the $[Ph_4P]^+$ salt, giving rise to the hypothesis that complexity of i.r. spectra is due to the interaction of $Co_2(CO)_8$ and $[Co(CO)_4]^-$ (when nothing else is present), and additional interactions when small cations (e.g. Na^+, Li^+) are used.

To some extent the cation also affects the rate of disproportionation in T.H.F. i.e. Li^+ and Na^+ are much faster than $[nBu_4N]^+$, but does not affect the equilibrium of products or intermediates. This is indicative of either a solvation effect or the degree of dissociation of the halide salt in solution, i.e. Li^+Br^- dissociates more fully than $[n\text{-}Bu_4N]^+Br^-$. Under certain circumstances, e.g. incompleteness of disproportionation, a poisoning effect is postulated. Two different routes have been visualised: (a) free Co^{2+} from the partial disproportionation poisoning the reaction or (b) Co^{2+} removing free halide from solution and so halting reaction. Experimental evidence which has been presented suggests that it is route (b) that is responsible, i.e. a build up of Co^{2+} after the initial reaction interacts with the free halide, stopping the progress of the reaction. To confirm this line of argument, the experiments using $Co(BF_4)_2$ in T.H.F. were carried out, the bulky $[BF_4]^-$ anion giving the effect that there is free Co^{2+} in solution. On $[Co(CO)_4]^-$ itself, present as $[Ph_4P]^+[Co(CO)_4]^-$, Co^{2+} has no effect at all, under carbon monoxide or nitrogen. With $Co_2(CO)_8$ under carbon monoxide there is slow disproportionation to $[Co(CO)_4]^-$ which can be hastened by use of nitrogen as the atmosphere. Thus Co^{2+}, if anything, is increasing the rate of reaction, rather than poisoning the reaction, corroborating the above statement that poisoning is due to removal of free halide from solution. The blank experiment was also useful in verifying the mechanism of Sternberg et al.[151] re disproportionation of $Co_2(CO)_8$ i.e.

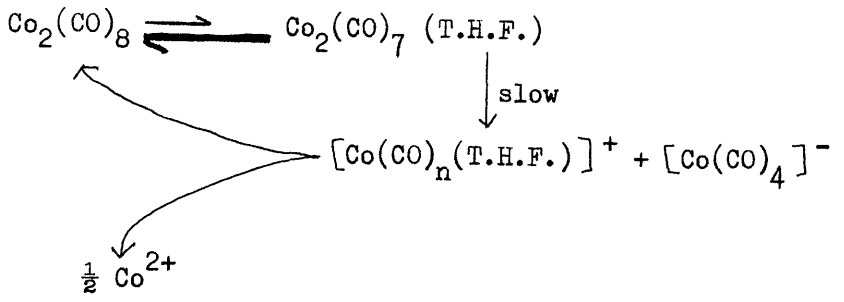


Figure 2.47

As Edgell has shown in great detail, there are three different ion pair sites in T.H.F. solutions. The relative occupation of these sites will vary according to temperature, solvent and pressure and so changes in i.r. spectra will be observed, with changes in line shape and wavenumber. There was not enough time for the present work to investigate this subject any further although a future project could provide valuable information.

A reaction mechanism for disproportionation is set out in Fig. 2.48.

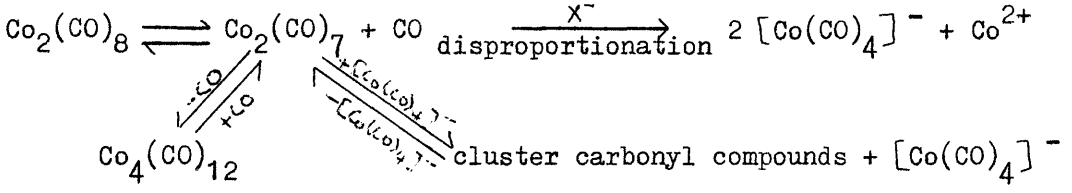


Figure 2.48

This can be expanded to show the role of the atmosphere:

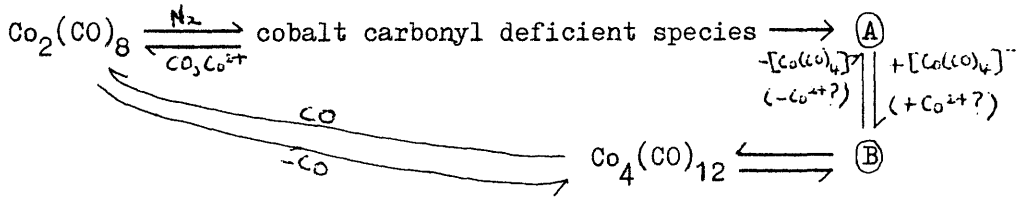
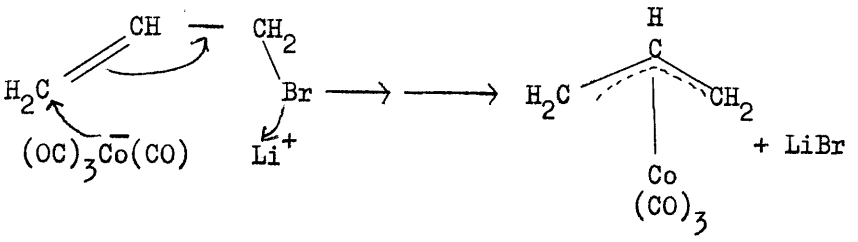


Figure 2.49

Species (A) and (B) are not identified, although anions such as $[Co_3(CO)_{10}]^-$ present under certain conditions could be assigned to either of them.

For the reaction involving allyl bromide, the complete inaction of $Co_2(CO)_8$ with it, together with the rapid removal of $[Co(CO)_4]^-$ if and when formed on addition of the lithium halide (removal of the anion was

so fast that its presence was not recorded on the i.r. spectrum) suggested the mechanism outlined below:



c.f.

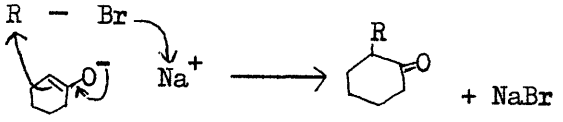


Figure 2.50

The high bonding power of Li^+ towards oxygen has often been observed e.g. the carbonyl bridged ion pair $Li[cpFe(CO)_2]$, whose existence is proved by i.r. absorption and relative concentration of the species in T.H.F. solutions of the salt, is much more reactive towards epoxides than the corresponding Na^+ salt. This is attributed to the more effective coordination of the epoxide oxygen by the lithium cation[231]. Further examples of the importance of Li^+ in stabilising certain cobalt carbonyl species will be presented in the following chapter.

It is interesting to note that reaction of $Co_2(CO)_8$ with T.H.F., under nitrogen, produce far larger quantities of $[Co_3(CO)_{10}]^-$ than $Co_2(CO)_8$ and NaBr in T.H.F. This is indicative of a better stabilising effect of Co^{2+}, in comparison with Na^+, with regard to $[Co_3(CO)_{10}]^-$ formation.

CHAPTER 3

FORMATION AND REACTIONS OF $[Co_3(CO)_{10}]^-$

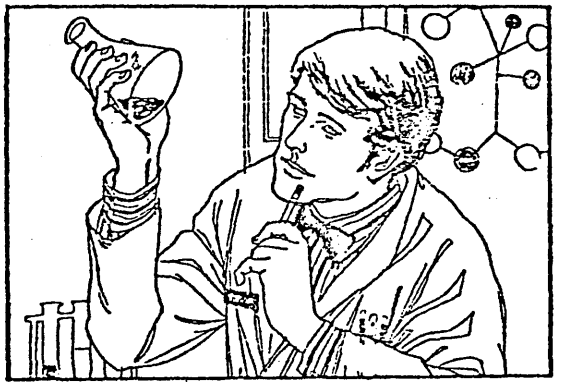
Chemistry of Carbon-Functional Alkylidynetricobalt Nonacarbonyl Cluster Complexes

236

DIETMAR SEYFERTH

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts

OR



I'll call it "Fred" 'cause alkylidynetricobalt nonacarbonyl's too damn long for me. [1]

[1] Claiming that it took longer to say "alkylidynetricobalt nonacarbonyl" than to make one, R. J. Spohn, who began our research program in this area, informally christened this compound class "Fred." Thus $ClCCo_3(CO)_9$ is chlorofred, $(OC)_9Co_3CCO_2H$, fredoic acid, $(OC)_9Co_3CC(O)CH_3$, acetofredone, etc.

CHAPTER 3 - THE FORMATION AND REACTIONS OF $[Co_3(CO)_{10}]^-$

1. INTRODUCTION

$[Co_3(CO)_{10}]^-$ is one of the more unstable cobalt carbonyl anions and as a consequence requires cations capable of interacting with it to stabilise the species. One such cation is lithium, Li^+. The stabilising influence is the ability of Li^+ to coordinate to the oxygen of the carbonyl species. Only in certain anionic or donor substituted carbonyl complexes is the carbonyl oxygen sufficiently basic to complex with Lewis acids. A prerequisite for such adducts is a high electron density on the carbonyl ligand (indicated by a low carbonyl stretching frequency i.e. below 1990cm $^{-1}$)[232]. This bonding by small cations is thought to be responsible for increasing the rate of decomposition of the formyl anion, $[Fe(CHO)(CO)_4]^-$ through the formation of ion pairs caused by the cation bonding to the formyl oxygen. This lowers the electron density on the metal which in turn decreases the π back bonding to the terminal carbonyls which increases the lability of the carbonyl ligands and so accelerates the decomposition.

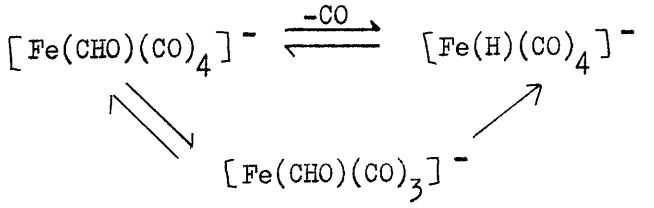


Figure 3.1

This high bonding power of lithium towards oxygen has been demonstrated in the higher reactivity of Li $[(\eta^5C_5H_5)Fe(CO)_2]$ towards epoxides, which can be contrasted with the corresponding Na^+ salt, because of Li^+ being more able to coordinate to the epoxide oxygen[232].

One further example of lithium's yearning for oxygen is displayed in lithium acyl tetracarbonyl ferrates (Li $[RCOFe(CO)_4]$). These will react with benzyl halides or acid halides to give unsymmetric ketones

in good yield[233] but the nickel analog, Li $[RCONi(CO)_3]$ give α-benzyl acyloins. Here the lithium-nickel compound is thought to be dinuclear in nature with bridging and terminal carbonyls as shown in Fig. 3.2.

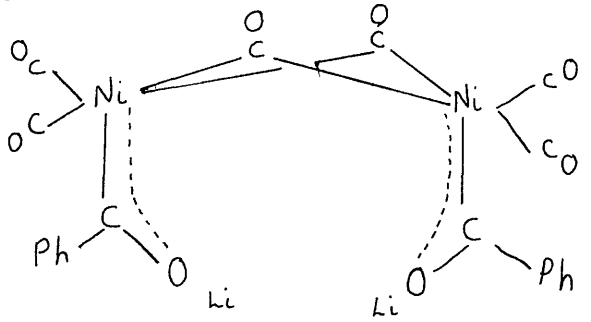


Figure 3.2

The preparation of $A^+[Co_3(CO)_{10}]^-$ (A = alkali metal, K, Na, Li) was first reported in 1970 from the reaction of alkali metals with $Co_2(CO)_8$ in diethyl ether[234]. (In THF, lithium and $Co_2(CO)_8$ react to give $LiCo(CO)_4$). The initial red crystals in solution turned black on removal of solvent and the solid Li^+ salt was shown to have the composition $LiCo_3(CO)_{10}$. The crystals will redissolve in diethyl ether to give a red solution. The i.r. of these compounds exhibit three distinct types of carbonyl bonds in the regions 2080-2000, 1850 and 1600 cm^{-1} which were assigned to terminal, doubly bridging and triply bridging carbonyl groups respectively, although the original report did not rule out an isomeric form containing no doubly bridging groups.

The compound was next isolated as the $LiCo_3(CO)_{10}.iPr_2O$ adduct with an X Ray diffraction determined structure[224]. The synthesis this time was reaction of $Co_4(CO)_{12}$ and $LiCo(CO)_4$ in di-isopropyl ether. Again discrete Li^+ and $[Co_3(CO)_{10}]^-$ molecules were found in the crystal with the cation tetrahedrally surrounded by one ether oxygen and three carbonyl oxygens of different clusters; the three cobalts

are arranged in a triangle. The i.r. absorption (in a nujol mull) around 1880 cm^{-1} was attributed to edge bridging carbonyl groups which were in equilibrium with isomers containing terminal carbonyls only when in an ether solution (evidence is from the extra weak absorption at 1865 cm^{-1}). The crystal structure of this compound is outlined in Fig. 3.3.

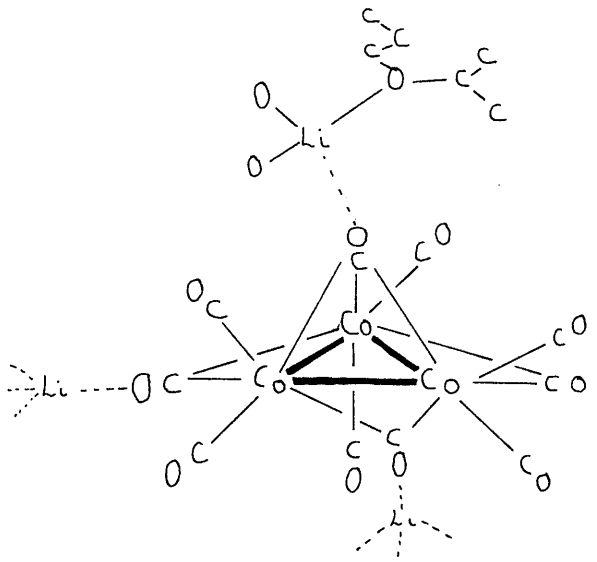


Figure 3.3

Cobalt structures based on an isosceles triangle are not uncommon, e.g. $Co_3\ \mu(CO)_3(C_5H_5)_3$ has a similar arrangement with each metal associated with a cp group and one carbonyl tripling bonding to all three cobalts. The other two ligands span two edges of the metal triangle, one asymmetrically and one semi-bridging[235]. Similarly, and even more closely related in structure are the class of compounds, $Co_3(CO)_9CR$ which are reviewed extensively[236].

The effect of the cation and the influence of the solvent is very marked in $[Co_3(CO)_{10}]^-$compounds. The optimum conditions for formation of such an ion are having Li^+ as the cation and n-dibutyl ether as the solvent, although analytically pure $LiCo_3(CO)_{10}\cdot\ Et_2O$ can be formed in diethyl ether[237]. The i.r. spectrum of the n-dibutyl

ether solution of $LiCo_3(CO)_{10}$ had carbonyl absorptions, $\bar{\nu}_{CO}$ at 2071w, 2006vs, 1999s, 1975m, 1865w and 1584 cm^{-1}. The delicate balance governing the existence of the compound is upset when carbon monoxide is passed over its solution with decomposition to $Co_2(CO)_8$ and $LiCo(CO)_4$ being the result. Removal of carbon monoxide from solution will reverse the reaction and so lead to the equation:

$$MCo(CO)_4 + Co_2(CO)_8 \rightleftharpoons M\,[Co_3(CO)_{10}] + 2CO \qquad (3.1)$$

Addition of 3% T.H.F. will have exactly the same effect on the equilibrium. Similarly it was shown that $Co_4(CO)_{12}$ and $LiCo(CO)_4$ in n-dibutyl ether, under argon, will produce $LiCo_3(CO)_{10}$ i.e.

$$2MCo(CO)_4 + Co_4(CO)_{12} \longrightarrow 2M\,[Co_3(CO)_{10}] \qquad (3.2)$$

As already shown, replacing lithium by sodium leads to substantially different results[212] i.e. loss of carbon monoxide from a solution of $Co_2(CO)_8$ and $NaCo(CO)_4$ gives $Co_4(CO)_{12}$. The present work will show that $[Co_3(CO)_{10}]^-$ is an intermediate stage in reactions of $Co_2(CO)_8$ and is only seen under conditions when the balance of competitive coordination by the counterion to the carbonyl groups or to the solvent is correct.

T.H.F. added to a n-dibutyl ether solution of $LiCo_3(CO)_{10}$, which has both the edge bridging and terminal carbonyl isomers present, results in considerable loss of the latter isomer from solution (from i.r. spectra) and modification of the spectral pattern associated with the face bridging carbonyl group at about 1580 cm^{-1}, while leaving the terminal region unaffected[224]. This is attributed to the loss of acidity of Li^+ caused by its coordination to the more basic T.H.F. The reactions examplified by equations 3.1 and 3.2 may be considered as redox reactions (w.r.t. the metal) or as oxidation - reduction involving one of the carbonyl groups (i.e. formation of a new Co-C (apical) bond). The next step was to synthesise the hitherto

unknown $Co_3(CO)_9C$-OH compound. This was achieved[238] by addition of excess dry hydrogen chloride to a stirred suspension of $LiCo_3(CO)_{10}$. Et_2O in hexane at -20°C to give a dark red solution with a characteristic i.r. spectrum, $\bar{\nu}$ co : 2090m-w, 2040vs, 2025s, 2000m and 1995w,sh cm^{-1} (c.f. $Co_3(CO)_9C$-OMe where the reported i.r. spectrum in carbon tetrachloride is[239] : 2108m, 2065vs, 2040s, 2020w and 1985m cm^{-1}). This compound at 40°C will convert to $HCo(CO)_4$ and $Co_4(CO)_{12}$ quantitatively (by i.r. inspection) via an unidentified carbonyl species (characteristic absorption at 1880 cm^{-1}) i.e.

$$2Co_3(CO)_9C\text{-}OH \longrightarrow 2HCo(CO)_4 + Co_4(CO)_{12} \qquad (3.3)$$

This was thought to be the first example of hydrogen migration from a carbonyl oxygen to the metal within the metal carbonyl complex. Since $HCo(CO)_4$ is in equilibrium with $Co_2(CO)_8$ and hydrogen (H_2)[64] the reverse of equation 3.3 may be regarded as the reduction of a coordinated carbonyl group by molecular hydrogen.

The isoelectronic iron compound, $H_2Fe_3(CO)_{11}$ has been isolated and found to contain both oxygen bonded and iron bonded hydrogen atoms[240].

Equation 3.3 can be brought about at room temperature using a closed vessel[241], involving oxidation of a $\rightarrow$C-OH group to coordinated carbon monoxide and the mystery species (at 1880 cm^{-1}) was identified as $HCo_3(CO)_9$. i.e.

$$Co_3(CO)_9C\text{-}OH \longrightarrow CO + HCo_3(CO)_9 \qquad (3.4)$$

The hydrido cluster, containing both terminal and bridging carbonyls, is easily decomposed by heat (30°C) and in solution forms $Co_4(CO)_{12}$. Addition of carbon monoxide at room temperature leads to formation of $HCo(CO)_4$ and $Co_4(CO)_{12}$ with some $Co_2(CO)_8$ depending on the amount of carbon monoxide present.

The latest work on this topic concerned the host of clusters which can be formed from $HCo(CO)_4$[242]. By careful removal of the gas evolved

at the appropriate temperature, $HCo_3(CO)_9$ (an electron unsaturated hydrido cluster) can be obtained. Varying the temperature between 0^o and 40^oC, the concentration of $HCo(CO)_4$ and the carbon monoxide pressures between 0-1 bar did not produce the acid derivative $Co_3(CO)_9COH$, only $HCo_3(CO)_9$ or $Co_4(CO)_{12}$. Typical reactions are shown in Fig. 3.4

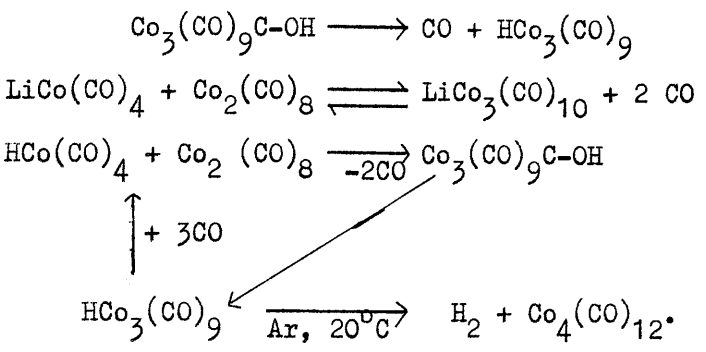


Figure 3.4

The formation of tri-nuclear cluster from $HCo(CO)_4$ is by attack of the H^+ at a carbonyl group of $Co_2(CO)_8$, the first example of reversal of hydrogen migration. These low nuclearity clusters would be, under different conditions, intermediates in homogeneous processes e.g. hydroformylation or reduction of carbon monoxide to methanol. $HCo(CO)_4$ can also act as a proton or hydride donor[243] depending on the solvent and reaction partners. With low polarity solvents tertiary amines and edge bridging carbonyl groups are believed to enhance the proton activity of $HCo(CO)_4$. e.g.

$$NEt_3HCo(CO)_4 + Co_2(CO)_8 \longrightarrow Co_3(CO)_9C\text{-}OH + NEt_3 + 2CO \qquad (3.5)$$

This is the first instance of an amine assisted transformation of a metal bonded hydridic hydrogen into an oxygen bonded hydrogen. The solution structure of the acid species has been determined[244] by ^1H n.m.r. and i.r. spectroscopy (Fig. 3.5).
(terminal carbonyl groups omitted for clarity).

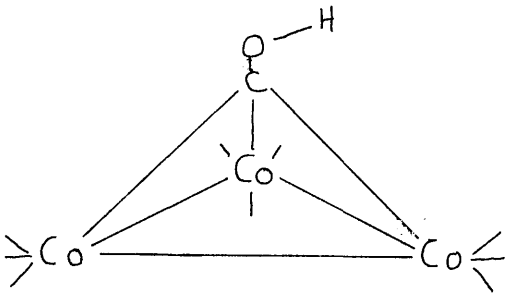


Figure 3.5

The crystal structure showed that each cobalt is bonded to three terminal carbonyls with the metal atoms in a regular triangle which is converted into a tetrahedron by inclusion of the apical carbonyl group. Similar Co-C and C-O distances, as found in $LiCo_3(CO)_{10}.iPr_2O$, exist in this compound but the hydrogen atom position could not be determined accurately, being inferred from the long C-O bond length of the apical carbonyl and the short O-O distance between two apical oxygen atoms (suggesting intermolecular hydrogen bonding). The long C-O bond (1.33A) is the largest carbonyl distance for metal coordinated carbon monoxide (the average C-O distance being 1.15A).

In solvents, $HCo_3(CO)_{10}$ behaves as a discrete molecule with no important intermolecular interactions (evidence for this is supplied by the compound's high solubility in hydrocarbons) and it is suggested that it could be used as a model for hydrogenation of carbon monoxide to methanol in a homogeneous phase, or even be a true intermediate of the reaction. The multisite interactions of the solid state, similar to the $Li^+ [Co_3(CO)_{10}]^-$ interactions, could qualify it as a model for hydrogenation of carbon monoxide in the heterogeneous phase.

Other indulgences of $[Co_3(CO)_{10}]^-$ in reactions has been pursued. With Me_3NBH_2I, replacement of I^- by the cobalt species occurs[245] (identified by elemental analysis and infrared spectroscopy), i.e.

$$NaCo_3(CO)_{10} + Me_3NBH_2I \xrightarrow{\text{toluene}} Me_3NBH_2\text{-}OCCo_3(CO)_9 + NaI \qquad (3.6)$$

The lithium salt will react with trimethylchlorosilane and the corresponding phenyl derivative to give siloxy derivatives in low yield:

$$R_3SiCl + LiCo_3(CO)_{10} \xrightarrow{Et_2O} R_3Si\text{-}OCCo_3(CO)_9 + LiCl, \quad R = Me, Ph \quad (3.7)$$

These experiments vindicated the assumption that the C-O bond order (of the triply bridging group) was low absorbing around 1600 cm^{-1}, with the negative charge localised on the oxygen, so because of the alkoxide character of this group, reaction is by nucleophilic displacement of halides from the appropriate species. These reactions were the first nucleophilic displacement reaction by the anion, although Lewis base activity by the carbonyl group of coordinated carbon monoxide was already known[246].

With halophosphines $LiCo_3(CO)_{10}$ reacted, but not as forecast[247] i.e.

$$[(CO)_9Co_3COLi] + ClPPh_2 \not\longrightarrow (CO)_9Co_3COPPh_2 + LiCl \quad (3.8\ a)$$

but $$[(CO)_9Co_3COLi] + ClPPh_2 \longrightarrow Ph_2PCo(CO)_4 + LiCl + \ldots\ldots \quad (3.8\ b)$$

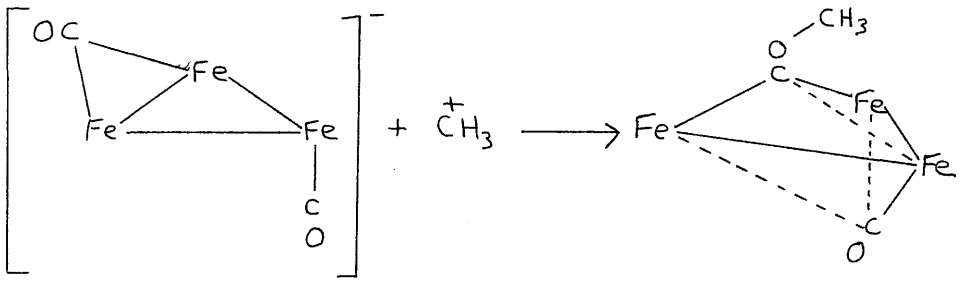
The Lewis acidity of the phosphorus halide towards the bridging carbonyls is not large enough to enable P-O interactions to take place and so P-Co derivatives are favoured. As this work was published before the findings of Fachinetti[237] the presence of $[Co(CO)_4]^-$ in solution puzzled the investigators. They favoured establishment of an equilibrium (as shown in equation 3.9) on the basis of evidence of $Co_2(CO)_6$ in solution (unpublished results of the authors - see ref. 247). Perhaps the halide anion is catalysing a reaction of $[Co_3(CO)_{10}]^-$ to give $[Co(CO)_4]^-$ [225].

$$[(OC)_9Co_3CO]^- \underset{}{\overset{solv}{\rightleftharpoons}} [Co(CO)_4]^- + Co_2(CO)_6(solv)_n \quad (3.9)$$

The atmosphere used in such experiments is not mentioned.

$LiCo_3(CO)_{10}$ will also react with $(cp)M(CO)_3Cl$ [M = Mo, W] to give a mixture of $(cp)(CO)_3MCo(CO)_4$ and $(OC)_9Co_3M(CO)_2(cp)$ [248].

These reactions of $[Co_3(CO)_{10}]^-$ are not unique to cobalt compounds. $[Fe_3(CO)_{11}]^{2-}$ (isoelectronic with $[Co_3(CO)_{10}]^-$) will react with electrophiles to give O - alkyl or O - acetyl derivatives of $[Fe_3(CO)_{10}(COR)]^-$ with the hydrido species $[HFe_3(CO)_{11}]^-$ giving $HFe_3(CO)_{10}(COR)$[249]. Earlier $[HFe_3(CO)_{11}]^-$ had been shown to form $HFe_3(CO)_{11}Me$ (using $MeSo_3F$ as the methylating reagent)[250]. The triangular array of iron atoms has one edge bridged by a carbonyl (presumably the same edge is bridged by the hydrogen atom in $[HFe_3(CO)_{11}]^-$ [251]) and the methyl group attached to the oxygen of the bridging carbonyl, the first time this had been observed. i.e.



$[HFe_3(CO)_{11}]^-$ $[HFe_3(CO)_{10}(COCH_3)]$

Figure 3.6

Theoretical calculations, of course, should not be forgotten. The highest occupied molecular orbital (H.O.M.O.) and the lowest unoccupied molecular orbital (L.U.M.O.) nature of metal - metal bonds have come to the attention of the theorists who employed electrochemistry, X Ray and electron spin resonance (e.s.r.) on metal - metal interactions to confirm the significant energetic separation of the M - M and M - L bonds (L = ligand)[252]. The compounds under scrutiny were the clusters illustrated in Fig. 3.7.

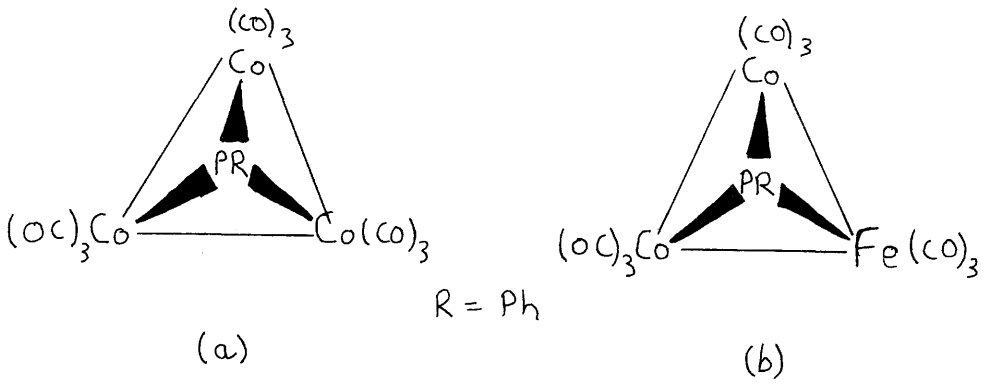


Figure 3.7

(a) has nineteen electrons whereas (b) has a closed electron shell. The extra electron of (a) makes the H.O.M.O. antibonding w.r.t. metal-metal interactions and this is borne out by the resultant lengthening of M - M bonds, with the same molecular geometry. Oxidation of (a) to give the monocation and reduction of (b) to give the monoanion are chemically and electrochemically reversible, proving that occupation of the first antibonding orbital (equivalent to H.O.M.O. in (a) and L.U.M.O. in (b)) does not effect decomposition (both decompose with excess oxidation) but that this is brought about by the emptying of the highest bonding orbital (H.O.M.O. in the cation form of (a) and in (b)). E.s.r. confirms the similarity of the two H.O.M.O. and shows no coupling with the phosphorus atom (i.e. the hyperfine coupling is too small to be observed). This is taken as proof of the H.O.M.O. of (a) and L.U.M.O. of (b) being (almost) exclusive combinations of metal d orbitals.

Part of the excitement generated by $[Co_3(CO)_{10}]^-$, and similar clusters, is anticipation of these compounds as an intermediate stage between coordination compounds and solid state chemistry. Especially w.r.t. the larger clusters molecules e.g. $[Pt_{26}(CO)_{32}]^{4-}$, $[Rh_{22}(CO)_{35}]$ etc., the crystal structures are beginning to resemble the close packed, infinite lattices of metals and alloys[253] and so study of such compounds may well lead to a better understanding of bulk metal chemistry.

Not only will $[Co_3(CO)_{10}]^-$ be studied, but later in the chapter the formation of $LiCo(CO)_4$ will be of interest. At present various preparations are in use e.g. reaction of short lengths of lithium wire with $Co_2(CO)_8$ in anhydrous T.H.F. (between -10^o and -20^oC). This is a vigorous reaction which subsides after twenty or thirty minutes[160]. Another route is formation of the sodium salt, $NaCo(CO)_4$ and then exchange with Li^+ (preferably not using sodium amalgam in the reduction step because of contamination) or by using lithium alkylborohydride cleavage[165]. Powdered sodium hydroxide will give $NaCo(CO)_4$ in a water containing solution[254]. Removal of solvent gives a white powder which can be redissolved in anhydrous T.H.F. ready to undergo exchange. As will be demonstrated, the reaction involving $Co_2(CO)_8$ and sodium hydroxide in diethyl ether is slightly more complicated although the desired product is reached in the end.

2. FORMATION OF $[Co_3(CO)_{10}]^-$ AS AN INTERMEDIATE IN DISPROPORTIONATION REACTIONS

As previously noted, $Co_2(CO)_8$ in diethyl ether gave a modified version of $Co_2(CO)_8$ in solution, slowly decomposing to $Co_4(CO)_{12}$ with no obvious intermediates (Changes in the terminal region are due to the overlapping absorbances of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ which will be comprehensively discussed in chapter 6.).

The initial hint of a new cobalt carbonyl species came in experiments involving $Co_2(CO)_8$ and LiBr in diethyl ether under carbon monoxide. Disproportionation to $[Co(CO)_4]^-$ was much slower than in T.H.F. and new bands became apparent at 2005s, 1995m and 1975w-m. Later, after the work of Fachinetti in this area of research became available, these were assigned to $[Co_3(CO)_{10}]^-$, there being good agreement with recorded values[237] (the bond at 1865 cm^{-1} could not be observed because

of the bridging carbonyl of $Co_2(CO)_8$ absorbing around 1850 cm^{-1}; the band at 1584 cm^{-1} is outwith the range of the spectra recorded). $LiBH_4$ results were much the same. With NaBr, under carbon monoxide, there is a small amount of $[Co_3(CO)_{10}]^-$ present as well as $Co_2(CO)_8$ and $[Co(CO)_4]^-$ which grows on addition of LiBr (see Fig. 3.8).

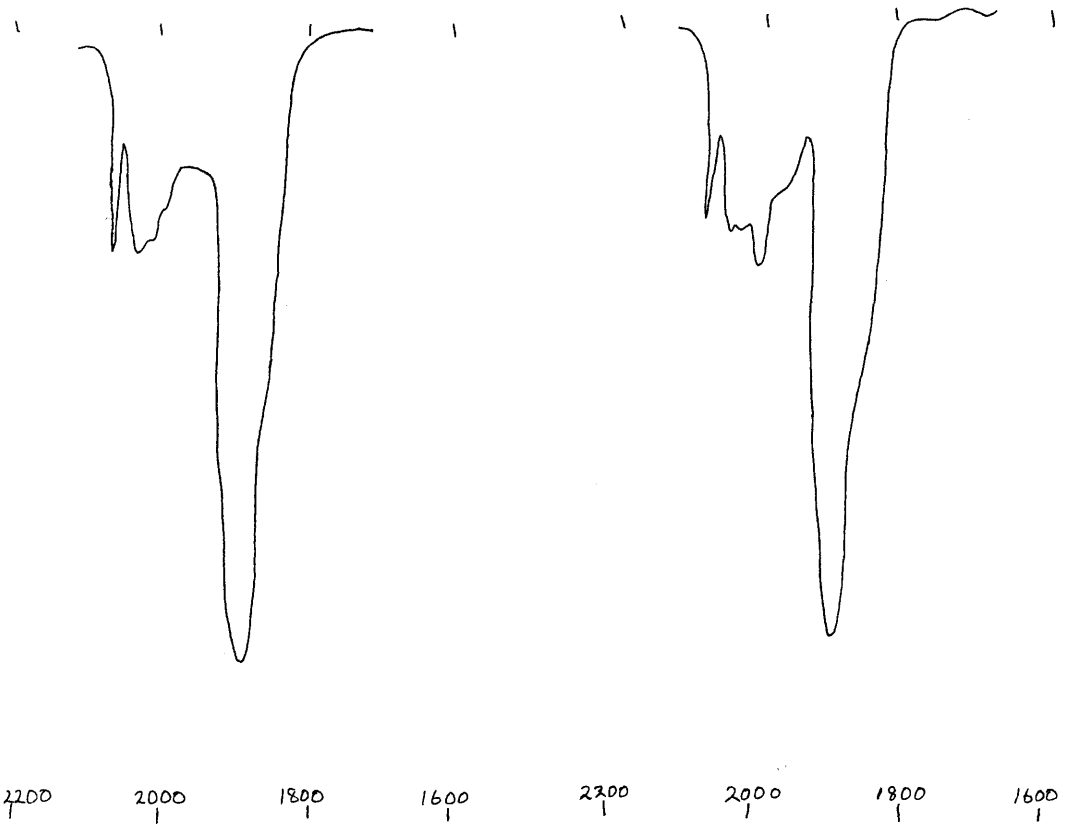


Figure 3.8

$[Co_3(CO)_{10}]^-$ can be an intermediate stage when $LiPF_6$ in diethyl ether and under nitrogen, is used as the catalyst.

In T.H.F. there were only two instances of formation of $[Co_3(CO)_{10}]^-$ both in nitrogen atmospheres: a) when $LiPF_6$ was reacted with $Co_2(CO)_8$ and b) $Co_2(CO)_8$ alone. The slowness of the first reaction (due to solvation problems?) enables the intermediate stages to be observed and so the reaction sequence described in Fig. 3.9a is easily followed. (For experimental details of this section, see chapter 2).

For b) the sequence is shown in Fig. 3.9b.

a) $Co_2(CO)_8 \longrightarrow Co_2(CO)_8 + [Co_3(CO)_{10}]^- + [Co(CO)_4]^- \longrightarrow$

$Co_4(CO)_{12} + [Co_3(CO)_{10}]^- + [Co(CO)_4]^-$

b) $Co_2(CO)_8 \longrightarrow Co_4(CO)_{12} + [Co(CO)_4]^- \longrightarrow [Co_3(CO)_{10}]^- +$

$Co_4(CO)_{12} + [Co(CO)_4]^-$

Figure 3.9

Presumably in b) $Co_4(CO)_{12} + [Co(CO)_4]^-$ recombine in some manner to give $[Co_3(CO)_{10}]^-$

3. FORMATION AND REACTION OF $Co_3(CO)_{10}^-$ USING ALKALI METALS IN DIETHYL ETHER

When an unsuccessful reaction of $Co_2(CO)_8$ in diethyl ether had been undertaken using mercury, $[Co_3(CO)_{10}]^-$ was present in solution. Again this was intermediate between $Co_2(CO)_8$ and the products, $[Co(CO)_4]^-$ together with some mercury - cobalt carbonyl species (to be discussed in chapter 4).

The reduction of $Co_2(CO)_8$ in diethyl ether proved difficult because of the many other species formed and it was felt that this warranted further attention.

Using sodium wire, a number of attempts were made to obtain $[Co_3(CO)_{10}]^-$ as the major species in solution. All of the experiments in this section were conducted under a carbon monoxide atmosphere (to simplify matters as far as possible).

Into a flask containing diethyl ether and sodium wire, was placed some $Co_2(CO)_8$ and the mixture stirred. Slow reduction (?) to $[Co_3(CO)_{10}]^-$ and $[Co(CO)_4]^-$ took place over twenty two hours giving a red-purple solution and the i.r. spectrum shown in Fig. 3.10 .

The signal at 1830 cm^{-1} is assigned to $[Co(CO)_4]^-$ (a suitable explanation will follow in the discussion at the end of the chapter). To complete the reaction (i.e. to obtain $[Co(CO)_4]^-$ in 100% yield) a little deionised, degassed water was added but proved a failure. Overnight, while both the carbon monoxide flow and stirrer were switched off the equilibrium between $[Co_3(CO)_{10}]^-$ and $[Co(CO)_4]^-$ shifted, favouring the former species. Switching both back on led to the equilibrium readjusting to favour the latter. This may be caused by a slow loss of carbon monoxide from solution, to favour $[Co_3(CO)_{10}]^-$ formation which is reversed on mixing the solution with the atmosphere making it richer in carbon monoxide.

When repeated using a weaker solution the reaction gave identical results i.e. a mixture of $[Co_3(CO)_{10}]^-$ and $[Co(CO)_4]^-$ is present. Slow addition of water immediately increased the concentration of both anionic species w.r.t. $Co_2(CO)_8$, with only the former present after twenty four hours.

Since water was required to make the reaction work, it was postulated that finely divided sodium hydroxide was the actual active reagent in anion formation (i.e. the reaction is disproportionation, not reduction). Finely ground down sodium hydroxide pellets (wet!) were added to $Co_2(CO)_8$ and within a day $[Co(CO)_4]^-$ (major species), $[Co_3(CO)_{10}]^-$ and traces of $Co_2(CO)_8$ were present (Fig. 3.11 a and b). The band at 1820 cm^{-1} in the earlier example (Fig. 3.10) is no longer distinct but appears as a shoulder of the main $[Co(CO)_4]^-$ signal. This is caused by the "wetness" of the solution - this assumption being justified by adding sodium wire, under argon, to give gas evolution (hydrogen) and an i.r. spectrum similar to that depicted in Fig. 3.10. It also favoured $[Co_3(CO)_{10}]^-$ w.r.t. $[Co(CO)_4]^-$ (See Fig. 3.11 c).

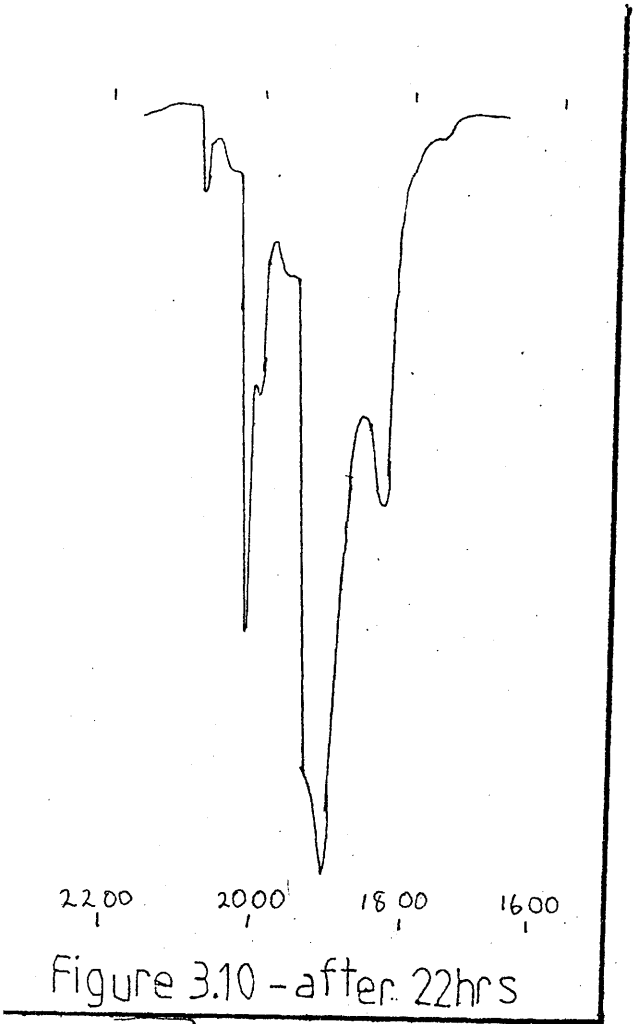
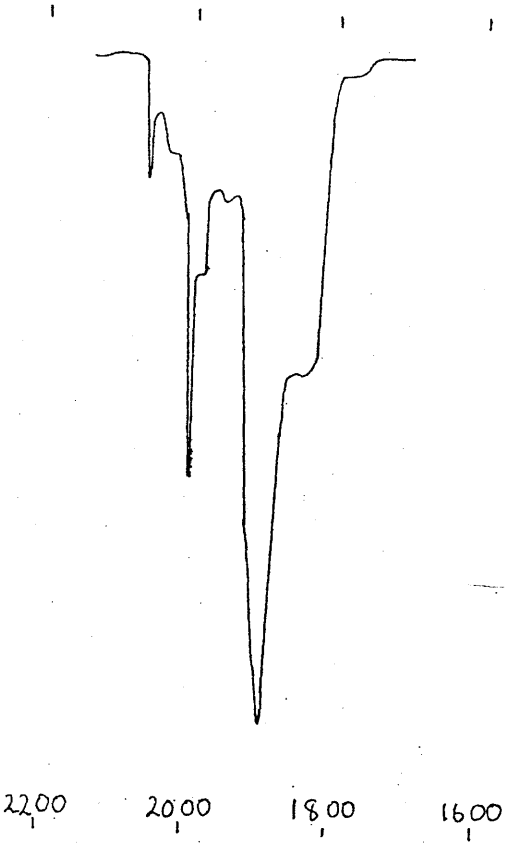
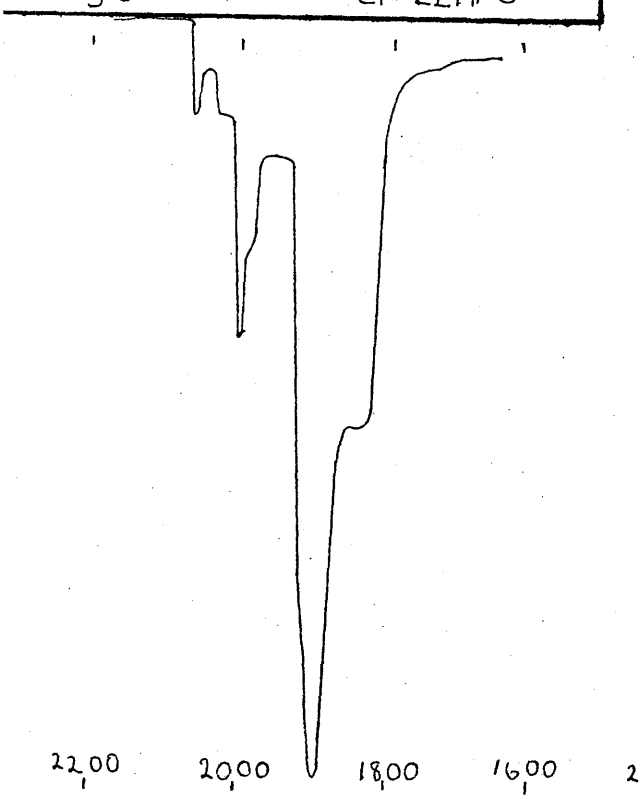


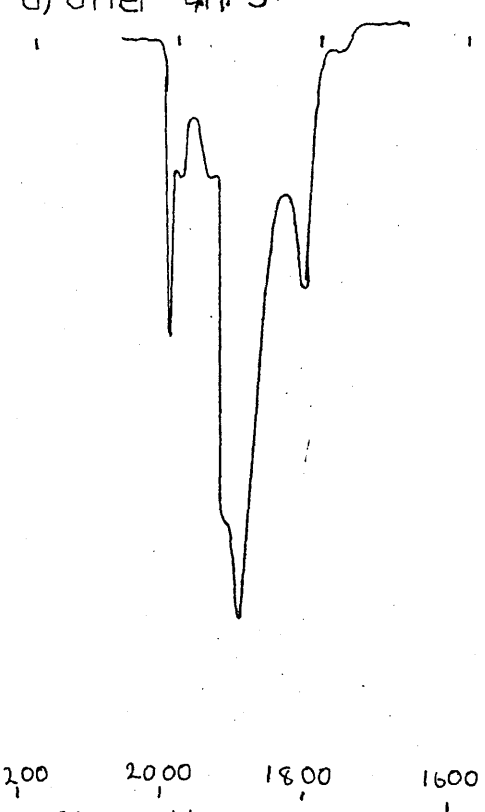
Figure 3.10 - after 22hrs



a) after 4hrs.



b) after 23hrs.



c) after 31hrs.

Figure 3.11

Having established that $[Co_3(CO)_{10}]^-$ and $[Co(CO)_4]^-$ co-existed in solution and the reaction was reproducable, the effects of different reagents on a) the ratio of $[Co_3(CO)_{10}]^-$: $[Co(CO)_4]^-$ and b) the physical effect of the cation on the $[Co(CO)_4]^-$ absorption frequency were tested.

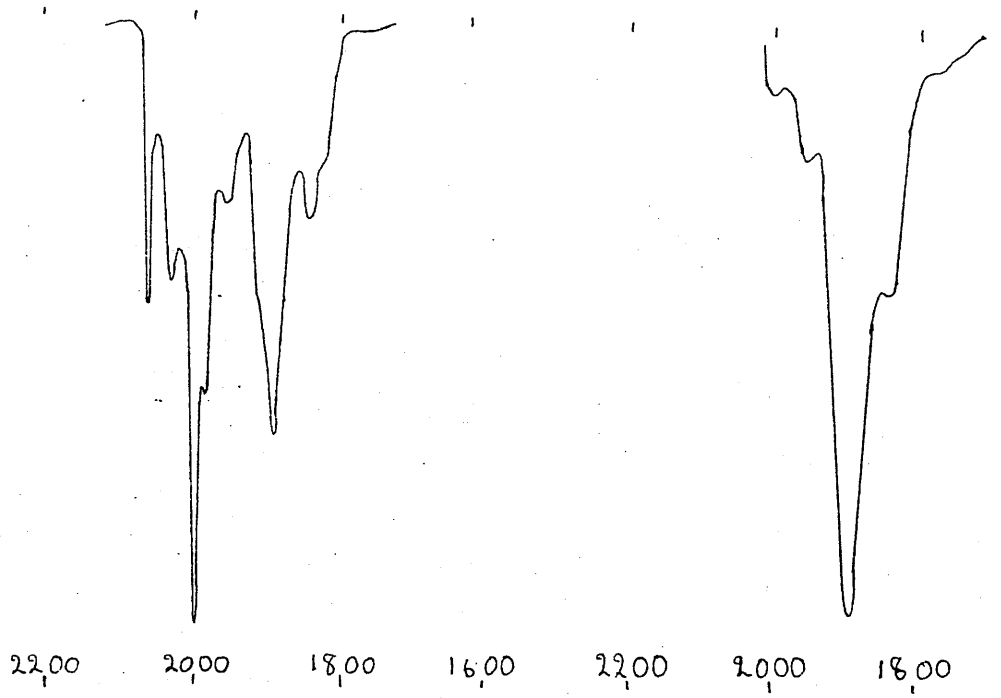
N, N, N', N' - tetramethylethylenediamine (T.M.E.D.) should "tie up" any cation and nullify its distortion of $[Co(CO)_4]^-$ or $[Co_3(CO)_{10}]^-$; in practice this was found to be the case. Within five minutes of stoichiometric aliquot of T.M.E.D. being syringed into the solution, the $[Co(CO)_4]^-$ signal had changed in character and disproportionation to this species virtually completed (see Fig. 3.12). i.e.

$$Co_2(CO)_8 + CO + [Co_3(CO)_{10}]^- \rightleftharpoons [Co(CO)_4]^- \qquad (3.10.)$$

When T.M.E.D. was added in stages, the disappearance of $[Co_3(CO)_{10}]^-$ and the change of signal of $[Co(CO)_4]^-$ could easily be followed.

Having demonstrated the susceptibility of $[Co(CO)_4]^-$ to its environment, it became mandatory to establish the "true" spectrum of the $[nBu_4N]^+$ and Li^+ salts. To this end, a mixture of $[Co_3(CO)_{10}]^-$ and $[Co(CO)_4]^-$ formed as described above and shown in Fig. 3.13a was split into different reaction vessels and large excesses of Bu_4NI and LiI added in turn, in a bid to displace Na^+ by preferential ionic exchange.

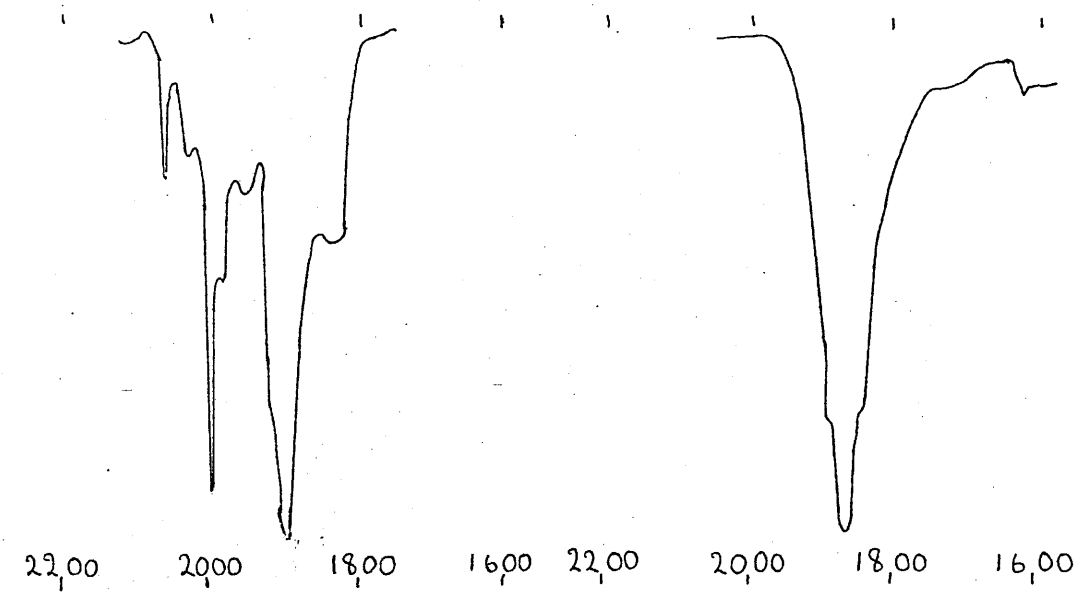
For nBu_4NI situation, the solution lightened in colour with a pale green solid being precipitated from solution. The i.r. spectrum confirmed what was suspected - that any $[Co(CO)_4]^-$ was being removed from solution by $[nBu_4N]^+$ as the solid salt, leading to further disproportionation of $Co_2(CO)_8$ and $[Co_3(CO)_{10}]^-$ to redress the balance, until no carbonyl species at all remained in solution. This took less than a day to reach completion. A nujol mull of the solid gave a spectrum of free $[Co(CO)_4]^-$ as shown in Fig. 3.13b.



a) after 25hrs.

b) 5min after TMED added

Figure 3.12



a) after 24hrs, + H_2O

b) solid after n-Bu_4NI added, nujul mull

Figure 3.13

Note that the main absorption is now at 1890 cm^{-1} i.e. the shift to 1910 cm^{-1} because of solvent effects has been nullified. Repeating this experiment using NaOH instead of sodium wire gave similar results. Addition of LiI led to spectacular changes in the i.r. spectrum. From the i.r. of solution prior to the addition (Fig. 3.13a) it changed to that shown in Fig. 3.13c within fifteen minutes, the signals at 1910 cm^{-1} and 1810 cm^{-1} both assigned to $[Co(CO)_4]^-$ perturbed by Li^+. Slow removal of $[Co_3(CO)_{10}]^-$ from solution followed within the next twenty hours. As for the nBu_4NI experiment, these results were also achieved using the NaOH produced solutions. The assignments of the i.r. frequencies were verified by using T.M.E.D. to complex Li^+ and the spectrum of the free $[Co(CO)_4]^-$ being obtained (see Fig. 3.13d,e,f). The initial amount of T.M.E.D. was enough to complex all Li^+ in solution but, although it hastened completion of the disproportionation to $[Co(CO)_4]^-$, conversion to free anion was not total (Fig. 3.13 d). Any Co^{2+} in solution would also complex with T.M.E.D. and when the extra amount of T.M.E.D. was added to compensate, the reaction sequence was completed, (Fig. 3.13 f).

Fired with enthusiasm, the experiments were repeated using lithium wire. In dry diethyl ether a very slow reaction takes place with only slight changes of the terminal carbonyl region of $Co_2(CO)_8$ (Fig. 3.14 a). Adding an adequate volume of water gave $[Co(CO)_4]^-$ with trace amounts of $Co_2(CO)_8$ and $[Co_3(CO)_{10}]^-$ within five minutes, the latter two species vanishing after half an hour. Controlled addition of water enabled the progress of conversion to be followed by infrared spectroscopy (Fig. 3.14 b and c). Fresh lithium wire dried the solution to give the now familiar spectrum of $LiCo(CO)_4$ (Fig. 3.14 d). When left to its own devices for a few days under a sealed carbon monoxide atmosphere the reaction displayed a penchant for reversal of

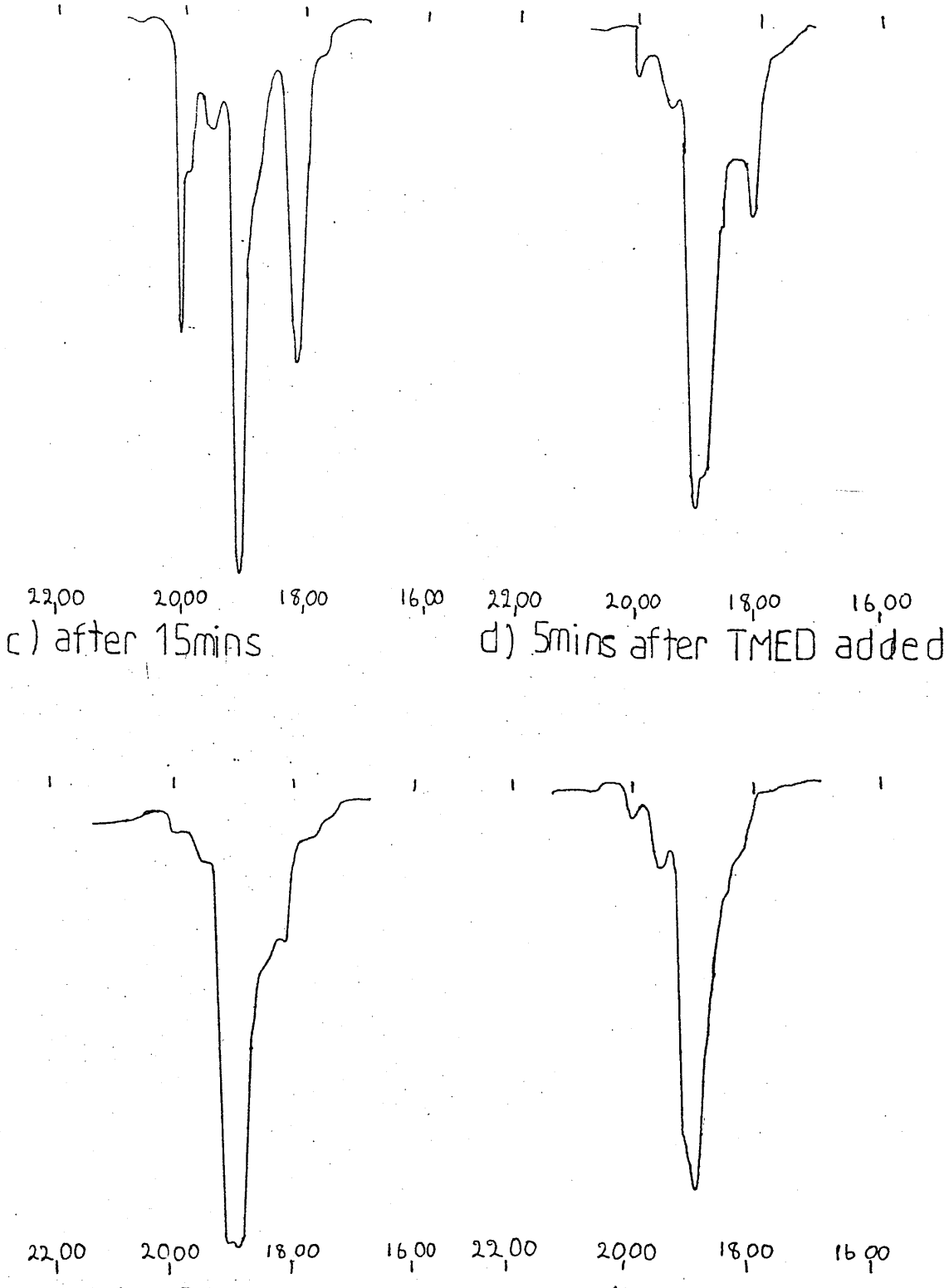


Figure 3.13 [cont.]

the equilibrium (equation 3.11) - see Fig. 3.14 e.

$$[Co_3(CO)_{10}]^- + [Co(CO)_4]^- \rightleftharpoons Co_2(CO)_8 \qquad (3.11)$$

This could be a result of air oxidation (see discussion).

If the solution of the wet anion (i.e. from the reaction of lithium wire and water with $Co_2(CO)_8$) is transferred to a new flask and fresh lithium added, some decomposition to $[Co_3(CO)_{10}]^-$ is noted. In a sealed system (i.e. no gas flow or stirrer) this will give $Co_2(CO)_8$ as the only carbonyl containing species.

These observations are all reproducible, the only change being the different ratios of species present in solution because of slight variations in the dryness of the ether and clean condition of the lithium wire.

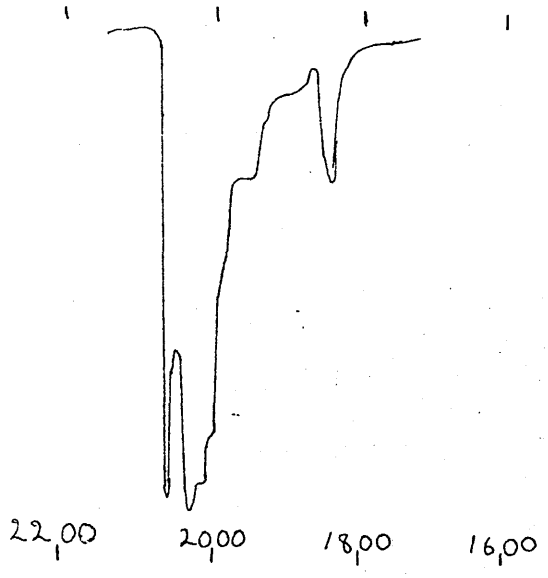
To complex Li^+, diglyme was added in controlled amounts to a solution containing both anions and lithium wire. As predicted, the absorbance frequencies of $[Co(CO)_4]^-$ shifted, coupled with slow completion of disproportionation.

An attempt to reproduce these observations using lithium hydroxide instead of lithium wire and water (c.f. sodium case outlined earlier) proved unfruitful; dissolution of LiOH in diethyl ether proving impossible, owing to the high lattice energy of the solid.

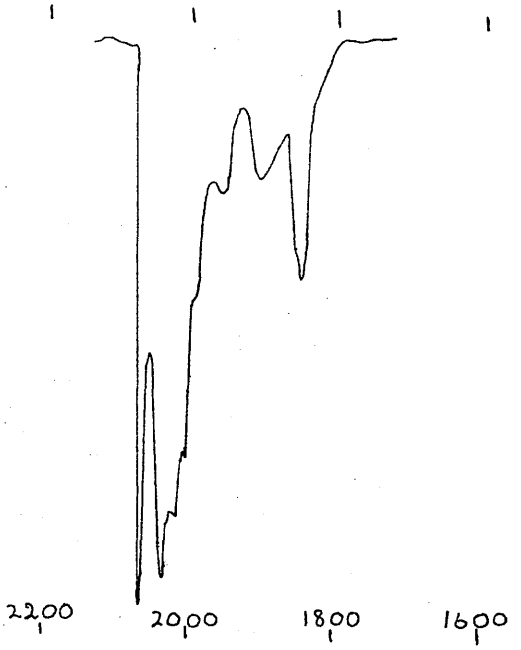
4. EXPERIMENTAL

1) Purification of T.M.E.D.

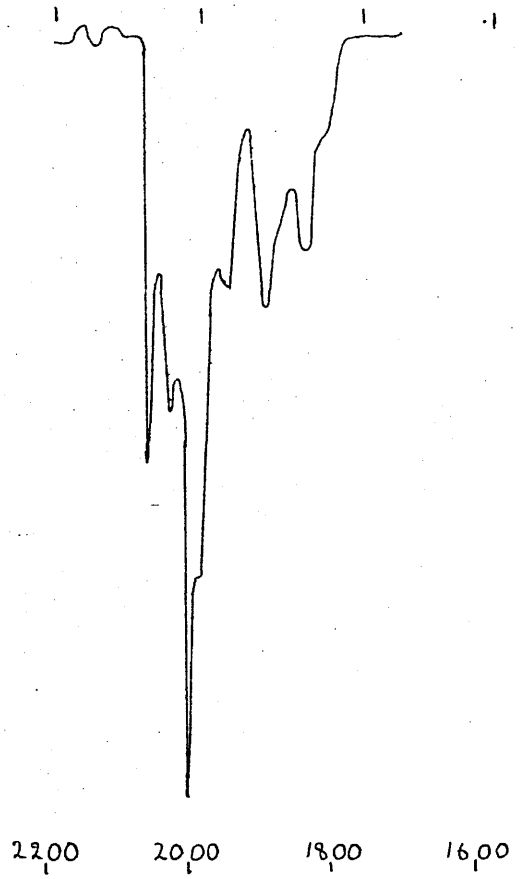
T.M.E.D. as supplied was a dark yellow liquid because of oxidised impurities. To remedy this, the liquid was shaken up with activated charcoal (to purify it) and with $MgSO_4$ (to dry it) for a few hours prior to use. Five minutes before being required, the mixture was filtered giving a very pale, almost clear, liquid which could be syringed into the reaction vessel. Any T.M.E.D. not used immediately was returned to the flask containing charcoal and $MgSO_4$ and the purification cycle restarted.



a) after 23hrs.

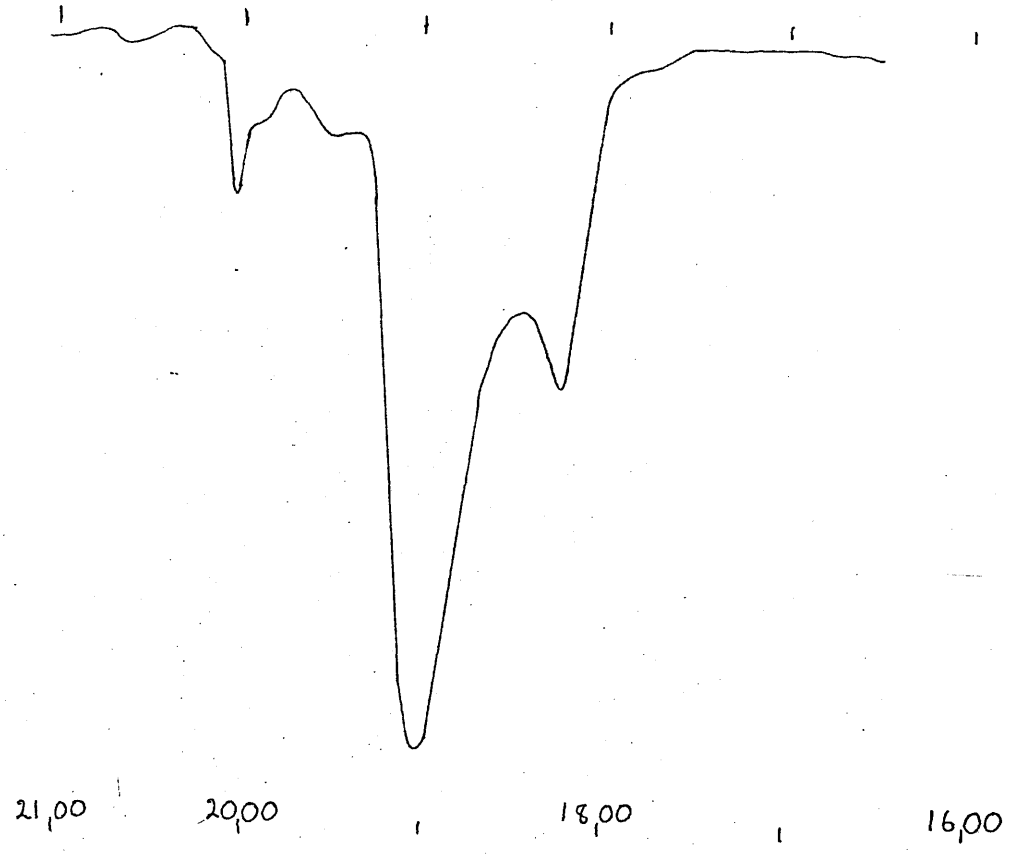


b) after 26hrs, + H_2O

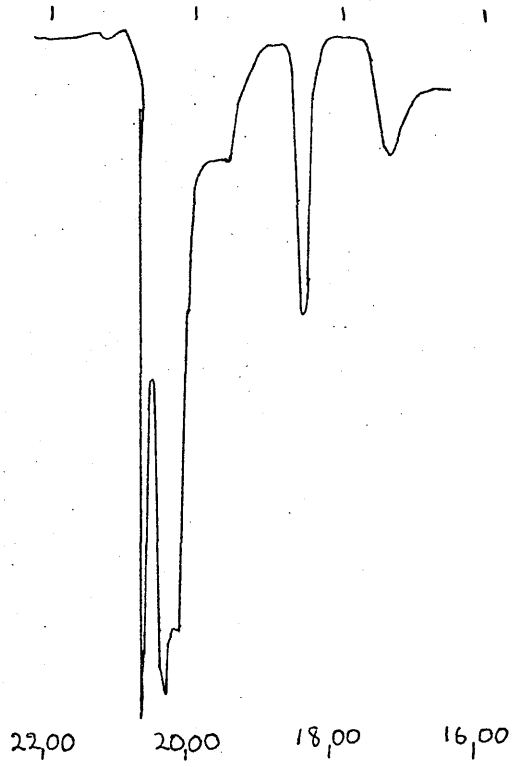


c) after 29hrs, + H_2O

Figure 3.14



d) $LiCo(CO)_4$



e) after 5 days, + H_2O

Figure 3.14 [cont.]

2) Reaction of $Co_2(CO)_8$ with Sodium Wire and Water.

All experiments requiring sodium or lithium wire were carried out in a specially designed flask. Because of problems associated with stirring such solutions, a link stirrer rod driven by a mechanical motor, was used. (In the literature for work involving lithium, a high speed stirrer with loose wire ends to act as cutters is recommended[160]). The flasks were three necked round bottomed vessels of 100 or 250 ml capacity, fitted with a run-off which had a teflon tap incorporated in it as well as a B14 cone at the end. Teflon taps were preferred since ethers tend to strip grease from a conventional tap; the cone enabled the solutions being drawn off to be transferred directly to another flask for further work. The necks of the flask contained the stirrer rod, and gas inlets and outlets. To obtain i.r. samples, the gas outlet was removed under an increased gas flow and an aliquot syringed from the flask. A diagram of the flask is given in Fig. 3.15. (I.r. spectra were run on the P.E.257 spectrometer unless specified otherwise).

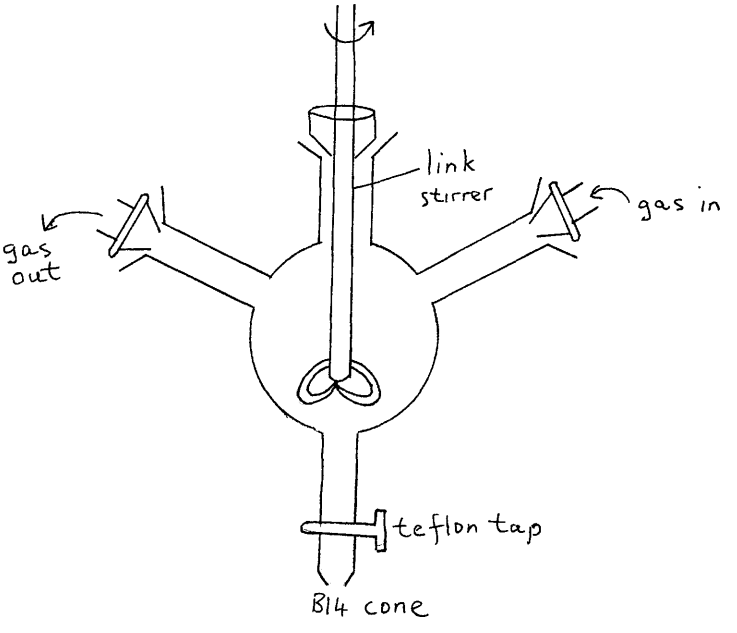


Figure 3.15

The solvent used in the experiments was only roughly dried using $MgSO_4$ since it was quickly established that water was needed to initiate a reaction.

Set out below is a detailed example of amounts of material required and colour changes noted in this type of reaction. This procedure was generally adhered to without variation.

Into the flask of Fig. 3.15 was poured 80 ml solvent. Sodium wire was added to the flask through the central part from a sodium press (having first removed traces of oil and dirt from the metal). At this stage normal atmospheric conditions prevailed in the flask. Connection to the carbon monoxide gas flow then followed and the stopper (in the central part) was replaced by the stirrer rod. After fifteen minutes the solution was deemed to be saturated with carbon monoxide and so approximately 0.3 g $Co_2(CO)_8$ [8.77×10^{-4} moles] was added. Within ten minutes the dark brown solution was red/brown and a few hours later the burgundy colour characteristic of the presence of $[Co_3(CO)_{10}]^-$ in solution was evident. About 300 μl deoxygenated, deionised water was added by syringe to increase the rate of conversion, resulting in an immediate gas evolution in the vicinity of the wire which gradually dulled in colour. (The water was deoxygenated, in vacuo, by freezing it, pumping down the flask, allowing to heat up to room temperature, then repeating the cycle two or three times. It was then removed and stored under nitrogen). After the reaction had reached a suitable point (with the equilibrium between $[Co_3(CO)_{10}]^-$ and $[Co(CO)_4]^-$ established) further sodium wire was added. This involved taking the flask to another part of the department, so it was closed, under carbon monoxide, transferred to the sodium press and the wire added against a counter-flow of argon, through the central port (the gas outlet remaining firmly shut). The vessel was then resealed,

taken back and reconnected to the carbon monoxide flow and stirrer. These elaborate precautions were necessitated by the extreme air sensitivity of cobalt anion solutions. Once the solution was thoroughly dried (as witnessed by infrared spectroscopy), it was filtered through dry siliconised glass wool placed between the tap and the cone of the run off (to remove any sodium oxidised solids or cobaltous precipitates) and under carbon monoxide flow, into ordinary 100 ml, three necked flasks (swept out with carbon monoxide beforehand) ready for further experimentation. Alternatively if for any reason filtration proved too difficult (e.g. the teflon tap became clogged) solutions were syringed into their new vessels under carbon monoxide. When larger quantities of the stock solution were required (e.g. when two or three independent experiments on the one solution were being conducted) 0.8 g $Co_2(CO)_8$ [2.34×10^{-3} moles] in 150-200 ml solvent was used.

3) Reaction of $Co_2(CO)_8$ with Sodium Hydroxide.

Into a 100 ml, three necked, round bottomed flask containing 80 ml diethyl ether was placed 0.219 g $Co_2(CO)_8$ [6.40×10^{-4} moles] and 0.143 g ground up (wet!) NaOH [3.58×10^{-3} moles.] This gave a white precipitate in solution while NaOH gradually dissolved. After four hours the solution was its typical burgundy colour with a little precipitate left, and was left for twenty four hours to stabilise. To dry the solution, sodium wire was added, under argon, as described in part (2) of this section, taking two hours to become reddish brown in colour with a pink precipitate (presumably cobalt carbonate[255]). The solution was filtered under carbon monoxide into a clean flask, ready for further reactions.

4) Reaction of $Co_2(CO)_8$ with Lithium Wire and Water.

The experimental apparatus and procedure were as outlined in part (2)

of this section with one minor deviation. Because lithium wire is more susceptible to reaction with air, it was added to the carbon monoxide swept flask containing the solvent under argon. A further purge with carbon monoxide was undertaken before 0.25 g $Co_2(CO)_8$ [7.31×10^{-4} moles] was added, giving a dark brown solution which changed to burgundy within a few hours. After 300 μl water was added, there was a gas evolution and greying of the lithium wire. Three hours later the solution contained a little $[Co(CO)_4]^-$ and a lot of $[Co_3(CO)_{10}]^-$. Filtration of the solution under carbon monoxide (to remove lithium wire and other solids) and leaving it at 0°C for two days resulted in the retrograde formation of $Co_2(CO)_8$. When a large excess of water is added (approximately 1 ml) only $[Co(CO)_4]^-$ results along with a purplish solid (c.f. the reaction with NaOH). This is accompanied by a lightening of solution colour to pale yellow. Further lithium wire will dry the solution and give the i.r. spectrum of $LiCo(CO)_4$ as shown in Fig. 3.14 d .

The above experiments were repeated using the Perkin-Elmer 335 spectrometer and gave identical results.

5) Reaction of $Co_2(CO)_8$ with Lithium Hydroxide.

0.03g finely powdered LiOH [1.25×10^{-3} moles] was dried, in the reaction vessel (i.e. a 100 ml, three necked round bottomed flask), in vacuo at 100°C overnight. The flask was cooled to room temperature under a nitrogen flow, then purged with carbon monoxide. 75 ml solvent was added to the flask followed by 0.23g $Co_2(CO)_8$ [6.73×10^{-4} moles] to give a brown solution and a white solid. Two days elapsed without change in the colour of the solution or the infrared spectra and so it was surmised that no reaction would occur.

6) Reaction of Solutions with Tetrabutylammonium Iodide.

A 40 ml portion of a 150 ml solution generated from 0.8g $Co_2(CO)_8$ [2.34×10^{-3} moles] was filtered into a three necked round bottomed

flask containing 0.6 g dried nBu_4NI [3.03×10^{-3} moles] . These quantities would make for a large excess of $[nBu_4N]^+$ in situ. The solution was pale orange with a green precipitate after fifteen minutes with a further paling of colour. The i.r. spectrum showed rapid loss of carbonyl species from solution and after twenty four hours only the green solid had cobalt carbonyl species present, with a colourless solution.

7) Reaction of Solutions with Lithium Iodide.

Another 40 ml fraction of the solution described in part (6) was filtered into a flask containing 0.31 g dried LiI [2.32×10^{-3} moles]. When drying LiI and in the initial part of its reaction, the container which it is in should be wrapped in aluminium foil to discourage light induced decomposition, detected by the pale yellow solid becoming much darker in hue. The reaction solution became light purple in colour with a purplish precipitate in fifteen minutes, the precipitate becoming blue/white after several hours. The i.r. spectrum after fifteen minutes already showed the distinctive spectrum of $LiCo(CO)_4$ with $[Co_3(CO)_{10}]^-$ present, the latter gradually being consumed overnight.

8) Addition of T.M.E.D. to Various Solutions.

To calculate the amount of T.M.E.D. required, it was assumed that two molecules of T.M.E.D. per Na^+ or Li^+ ion or three molecules per Co^{2+} ion in solution were required. For the reaction:

$$3Co_2(CO)_8 + 4Na/H_2O \longrightarrow 2Co^{2+} + 4NaCo(CO)_4 \xrightarrow{4LiI} 4LiCo(CO)_4 + 4NaI + 2Co^{2+} \quad (3.12.)$$

where 1.87×10^{-3} moles of $Co_2(CO)_8$ had been added, the maximum expected would be 2.5×10^{-3} moles Na^+ and 1.24×10^{-3} moles Co^{2+}. If the solution is halved (to conduct two different experiments) each would require 4.46×10^{-3} moles of T.M.E.D. which equates with 0.61 ml T.M.E.D. (molecular weight = 116 g, density = $0.8 gml^{-1}$). For the

experiment with LiI, a further 4×10^{-3} moles of T.M.E.D. was required to complex all Li^+ present (including the excess), which is a further 0.58 ml T.M.E.D.

These stoichiometric amounts of freshly distilled T.M.E.D. were syringed into the different solutions in stages. To the solution containing $NaCo(CO)_4$ and $[Co_3(CO)_{10}]^-$ addition of 370μl resulted in the solution becoming red/orange with a dense, light coloured, precipitate coming out of solution. A further 310μl T.M.E.D. only succeeded in making the colour of solution paler and the precipitate becoming pale yellow. Adding T.M.E.D. to a solution of $[Co_3(CO)_{10}]^-$, $[Co(CO)_4]^-$, Na^+ and LiI resulted in an intense purple coloured liquid phase and some white solid initially becoming dark green with the solid remaining. The passage of time brought about a pale green solution with more bluish/white precipitate forming, NaI contaminated with a cobalt iodide species.

5. DISCUSSION

The experiments being discussed here have proved beyond all doubt that $[Co_3(CO)_{10}]^-$ is an intermediate stage in the production of $[Co(CO)_4]^-$ from $Co_2(CO)_8$. It is favoured in less efficient donor solvents (i.e. diethyl ether is better than T.H.F. w.r.t. its lifetime) and with the smaller more highly polarised lithium cation. It is considered that in T.H.F. the solvent attack on $Co_2(CO)_8$, as well as the halide attack makes this transient state too short-lived to be observed. The stabilising effect of Li^+ was neatly illustrated when LiBr was added to a mixture of $Co_2(CO)_8$ and NaBr in diethyl ether which had nearly reached completion of disproportionation to $[Co(CO)_4]^-$ (i.e. only a little $[Co_3(CO)_{10}]^-$ was left). After LiBr was put in, the $[Co_3(CO)_{10}]^-$ signals grew in intensity and the final traces of $Co_2(CO)_8$ vanished (see Fig. 3.8).

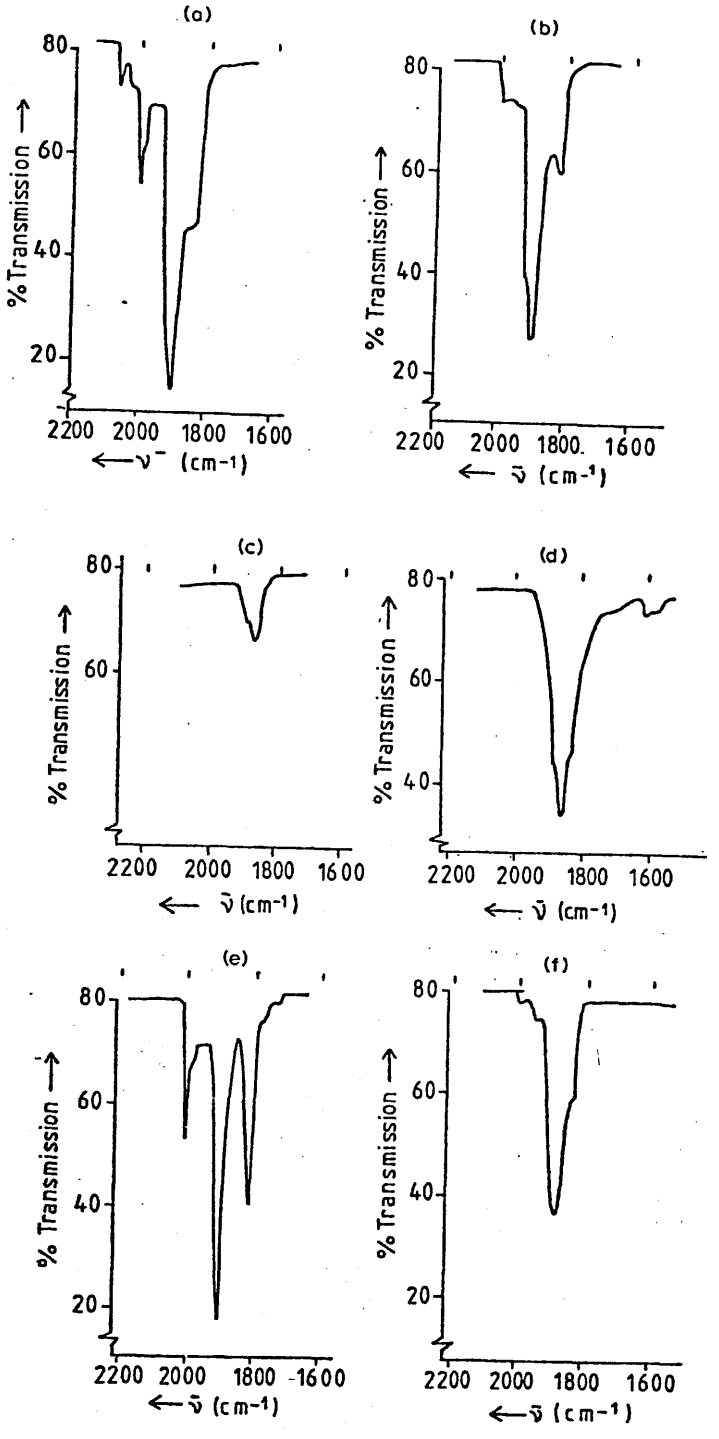
In these situations, any trace of moisture seems to destroy $[Co_3(CO)_{10}]^-$.

A similar result was seen earlier in the reaction of $Co_2(CO)_8$ with LiBr in diethyl ether. In rigorously anhydrous conditions it was very difficult to get beyond the stage of $[Co_3(CO)_{10}]^-$ and $[Co(CO)_4]^-$ co-existing but under wet conditions the concentration of $[Co(CO)_4]^-$ was markedly improved with a corresponding fall in the concentration of $[Co_3(CO)_{10}]^-$ (to almost zero). This was shown in Fig. 2.29.

Using sodium (or lithium) wire to obtain anionic species from $Co_2(CO)_8$ would seem to be mainly a disproportionation reaction rather than a reduction reaction since water is necessary to produce any significant progress towards anions. The conclusion reached was that sodium plus water formed finely divided NaOH which reacted in situ. Even with lithium wire, the reaction occurred, although using LiOH supplied by outside means could not reproduce the results. Under these circumstances water preferentially reacts with the alkali metal, not $[Co_3(CO)_{10}]^-$.

An attempt to reduce $Co_2(CO)_8$ by means of a sodium/copper reduction couple proved unsuccessful, perhaps because of insufficient contact between the two metals.

One pleasing aspect of this work was the manner in which the different cations and the extent of the elimination of water from solution could be demonstrated to affect the shape and frequency of the $[Co(CO)_4]^-$ absorption. For ease of reference these are summarised in Fig. 3.16. Solution A (Fig. 3.16 a) absorbs at 1890vs and 1830sh cm^{-1} and is as expected for weakly distorted, near tetrahedral $[Co(CO)_4]^-$ with some $[Co_3(CO)_{10}]^-$ still present in solution. This wet solution is dried over sodium wire to give solution B (Fig. 3.16 b). The 1890 cm^{-1} band now has a high frequency shoulder and a separate, clearly resolved band at 1825 cm^{-1}. (Similar spectra have been derived from the system



(a) Solution A: NaOH treated $Co_2(CO)_8$ in wet diethyl ether. Note $[Co_3(CO)_{10}]^-$ bands and modified $[Co(CO)_4^-]$ band.
(b) Solution B: as A, after drying and reduction with sodium wire.
(c) As B, after addition of $(n\text{-}C_4H_9)_4NI$. Note presence of both free and modified $[Co(CO)_4]^-$.
(d) Solid $[(n\text{-}C_4H_9)_4N][Co(CO)_4]$, Nujol mull.
(e) $LiCo(CO)_4$ ($+LiCo_3(CO)_{10}$) from addition of LiI to solution B.
(f) As e, after addition of TMED. Note disappearance (base induced disproportionation) of $[Co_3(CO)_{10}]^-$, and near-normal $[Co(CO)_4]^-$ band.

Figure 3.16

$Co_2(CO)_8$ / sodium amalgam / diethyl ether together with bands for $Hg[Co(CO)_4]_2$ and $\{Hg[Co(CO)_4]_3\}^-$ which will be discussed in the following chapter). The removal of water from solution has allowed tighter ion pairing between the cation and the anion and so the symmetry of the anion is lowered giving two i.r. absorptions. If $Co_2(CO)_8$ and sodium wire are used in wet diethyl ether the same effects are noted after a few hours (i.e. when the alkali metal has reacted with all the water). To obtain the free, tetrahedral, anion from solution B, all that is required is the presence of T.M.E.D. or some such chelating ligand to 'tie up' the cation to give a spectrum similar to Fig. 3.16 f .

Fig. 3.16 c and d show respectively the disappearance of carbonyl bands from the solution and these bands in the solid when $[nBu_4N]^+$ is the counterion. The main absorption in solution has moved to 1875 cm^{-1} with a weak band at 1890 cm^{-1} (the remaining $Na^+[Co(CO)_4]^-$ ion pair). Note that in the solid the two side bands on either side of the main absorption (at 1865 cm^{-1}) are due to solid state effects. As shown by the experimental work, other large organic cations e.g. $[Ph_4P]^+$ and $[Bu_4P]^+$ will precipitate the anion from diethyl ether solutions although all are soluble in T.H.F.

Addition of Li^+ to form $LiCo(CO)_4$ has the most significant effect on the i.r. spectrum (Fig. 3.16 e). There is a little contamination, due to $[Co_3(CO)_{10}]^-$ but the main signals at 1905 and 1815 cm^{-1} are due to $LiCo(CO)_4$. The more marked shift and splitting of the absorption (compared with Fig. 3.16 b) is because the smaller cation can, and does, indulge in more electron withdrawal and greater distortion of the anion. Three possible structures were envisaged (Fig. 3.17).

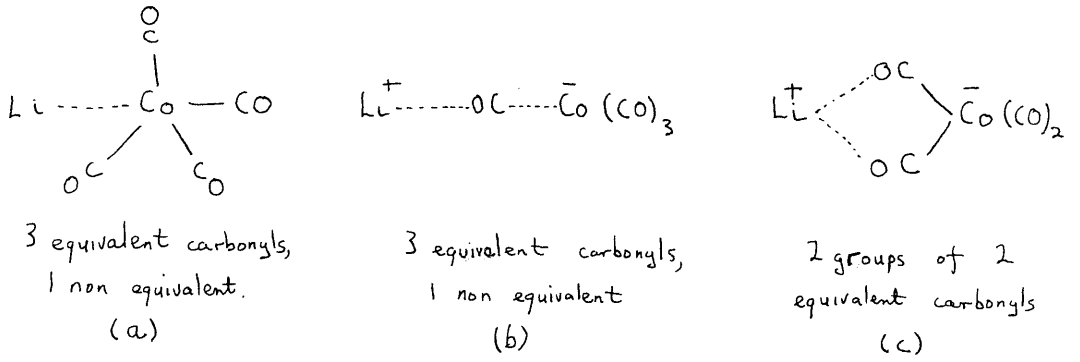


Figure 3.17

(c) was considered unlikely, from i.r. considerations, and the literature indicated that in $[Co_3(CO)_{10}]^-$ compounds, the Li^+ bonds to a carbonyl group[224]; in $LiMn(CO)_5$ it has been shown that Li^+ will bond to a carbonyl group rather than to the metal centre[215,216]. These observations are more consistent with structure (b) than with (a) or (c).

This can be contrasted with the recently published crystal structure of $Co_3(CO)_9CH$ which shows no edge bridging or triply bridging carbonyl groups, the molecule being C_3v symmetry with the three cobalts and the CH group forming a distorted tetrahedron[256].

To remove the disturbing influence of Li^+, T.M.E.D. will again prove adequate, giving the "free" anion as depicted in Fig. 3.16 f which closely resembles Fig. 3.16 b but at slightly lower frequency. Unexpectedly this reaction is not immediate, a gradual change being noted over a few hours. This can be compared with the effect of N,N^1 ethylenebis (salicylideniminate) (salen), which when compounded with $NaCo(CO)_4$ under carbon monoxide and in T.H.F. gave the complex ion pair $\{[Co(salen)]_2 NaCo(CO)_4THF\}$. By determining its crystal structure, Na^+ was found to be octahedrally coordinated by six oxygen atoms, from two Co(salen) groups (acting as bidentate ligands), T.H.F. and $[Co(CO)_4]^-$ bonded to Na^+ through one of the carbonylic oxygens.

The anion group has essentially undisturbed tetrahedral symmetry. This is a good example of using inorganic ligands (i.e. oxygens bonded to metals) to form a cage round an ion with the oxygens from different coordination species[223a].

Using lithium wire instead of sodium gave a mixture of $Li^+[Co_3(CO)_{10}]^-$ and $Li^+[Co(CO)_4]^-$ very slowly. Water spurs on the reaction with vigorous gas evolution (presumably hydrogen released by the action of water on lithium) and LiOH formed in situ which is responsible for hastening the reaction. The i.r. spectrum is of weakly perturbed anion (Fig. 3.16 a) which on drying out becomes that of the anhydrous $LiCo(CO)_4$ (Fig. 3.16 e). In the wet solution there are tetrahedral symmetry anions, $[Co(CO)_4]^-$, and solvated lithium cations. As water is removed from solution, by the metal, Li^+ can participate in tight ion pairing and in so doing alter the i.r. spectrum to that of Fig. 3.16 e. This is reminiscent of Edgell's work with solvated Na^+ and $[Co(CO)_4]^-$ in different solvents[205].

The i.r. spectra of Fig. 3.16 have their stretching frequencies summarised in Table 3.1 (see overleaf).

Sample[a]	$\bar{\nu}$(CO)(cm^{-1})(Species present)	Figure
Solution A	2005m, 1995m [$NaCo_3(CO)_{10}$] ; 1890s, 1830(sh) [$NaCo(CO)_4$]	1a
Solution B	1920(sh), 1890s, 1830m (dried $NaCo(CO)_4$)	1b
$[(n\text{-}C_4H_9)_4N][Co(CO)_4]$	1890w [$NaCo(CO)_4$] : 1875m $[\{(n\text{-}C_4H_9)_4N\}\{Co(CO)_4\}]$	1c
Solid $[(n\text{-}C_4H_9)_4N][Co(CO)_4]$ [b]	1885(sh), 1865s, 1840(sh) $[\{(n\text{-}C_4H_9)_4N\}\{Co(CO)_4\}]$	1d
$Li^+[Co(CO)_4]^-$	2005m, 1995w [$LiCo_3(CO)_{10}$] ; 1905s, 1815m [$LiCo(CO)_4$]	1e
TMED complex	1885s, 1860(sh), 1835(sh) (TMED complex of $[Co(CO)_4]^-$)	1f
Solution C	2070m, 2040m [$Co_2(CO)_8$] ; 2005s, 1995s, 1970m [$\{Co_3(CO)_{10}\}^-$] ; 1910s [$\{Co(CO)_4\}^-$] ; 1860m [$Co_2(CO)_8$ and $\{Co_3(CO)_{10}\}^-$] ; 1820m [$\{Co(CO)_4\}^-$]	2

[a]Solutions in diethyl ether, corrected for solvent background, 0.1 mm cell, sapphire windows.

[b]Nujol mull, NaCl plates.

Table 3.1

These observations can be contrasted with the reactions of metal carbonyl anions compounded with magnesium which will form metal - metal bonds with the coordination number of magnesium fulfilled by solvent molecules to give the general molecular formula of the complex as $B_xMg(M)_2$ where x = 2 or 4 depending on the base and M = metal carbonyl anion[257].

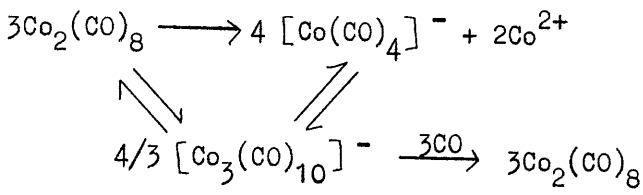
e.g. $(Fe(CO)_2cp)_2 + MgHg \xrightarrow{B} B_xMg[Fe(CO)_2cp]_2$, B = T.H.F., T.M.E.D.A. (3.13)

or $cpFe(CO)_2I + MgHg \xrightarrow{B}$ "$cpFe(CO)_2MgIxB$" $\xrightarrow{B} B_xMg[Fe(CO)_2cp]_2 + B_xMgI_2$ (3.14)

However for the cobalt complex $B_4Mg[Co(CO)_3L]_2$, B = T.H.F., pyridine or T.M.E.D.A., L = P or CO, the i.r. spectrum suggests no vibrational coupling between the $Co(CO)_4$ groups; the very low carbonyl frequency is at 1770 cm^{-1} which is taken to imply Mg-O = C-Co type bridging between the magnesium and the carbonyl.

An interesting diversion was provided in trying to calculate what was happening in the reaction of $Co_2(CO)_8$ with lithium wire (and water). When this was left, sealed under carbon monoxide, the equilibrium between the species in solution was upset (see Fig. 3.14 c and e) i.e. the two anionic species appeared to be recombining to form $Co_2(CO)_8$ in addition to themselves.

The most probable explanation is that there was a slight air leak in the system. The anionic species being more susceptible to air oxidation than $Co_2(CO)_8$ would react, with the carbon monoxide atmosphere, decaying to give $Co_2(CO)_8$. It was calculated that for the initial concentration of $Co_2(CO)_8$ present, and using Fig. 3.18 below, about 30% of the available carbon monoxide atmosphere was needed for complete conversion, i.e. this was the maximum possible amount which could be consumed.



i.e. 1 : 1 ratio of $Co_2(CO)_8$: carbon monoxide required.

Figure 3.18

Any consumption of carbon monoxide would reduce the pressure inside the reaction vessel and so favour any air leak.

Switching on the carbon monoxide flow and stirrer again would saturate the solution and exert its influence upon the equilibria in force, causing a further readjustment.

Studies of air oxidation of manganese carbonyl substituted compounds $[Mn_2(CO)_{10-x}L_x$, x = 1 or 2] would seem to confirm this attitude. $Mn_2(CO)_{10}$ in decalin will decompose to manganese(IV) oxide with oxygen. There was also oxidation of the solvent to ketonic products (as witnessed by infrared spectroscopy)[258]. Under air the reaction is approximately first order in $Mn_2(CO)_{10}$ this falling to 1/2 order as the concentration of the carbonyl compound increases. Under pure oxygen first order is maintained until high concentrations, under 5% oxygen, 1/2 order is maintained to low concentrations; The proposed mechanism is :

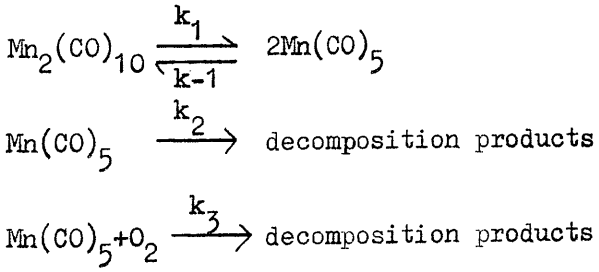


Figure 3.19

With the substituted derivative $[Mn(CO)_4(PPh_3)]_2$ decomposition in oxygen is 70% faster than the substitution reaction of carbon monoxide.

For a 1:1 ratio of oxygen : carbon monoxide, the rate of substitution of one PPh_3 by CO is identical to the rate of substitution in carbon monoxide alone[259]. The reaction mechanism proposed is shown in Fig. 3.20.

$$[Mn(CO)_4(L)_2]_2 \rightleftharpoons 2[Mn(CO)_4L] \qquad (a)$$

$$[Mn(CO)_4L] + O_2 \rightleftharpoons \text{decomposition} \qquad (b)$$

$$L = PPh_3$$

Figure 3.20

with (b) inhibited by carbon monoxide.

For the monosubstituted species $Mn_2(CO)_9L$, the equality of rates of reaction with oxygen and Ph_3P and the sensitivity to even small amounts of carbon monoxide suggest a CO dissociative mechanism following homolytical fission.

It may well be that free radical species e.g. $\cdot Co(CO)_3$ or $\cdot Co(CO)_4$ are involved in the decomposition reactions of cobalt carbonyls.

A brief resume of the reactions discussed involving sodium wire is given in diagramatic form in Figs. 3.21 and 3.22.

Unfortunately (!) time did not allow for investigation of these reactions under nitrogen. Carbon monoxide was used in preference to nitrogen for reasons outlined at the beginning of section 4, but it is expected that similar behaviour will occur under nitrogen with a greater tendency to form carbonyl deficient clusters which will complicate the i.r. spectra even more.

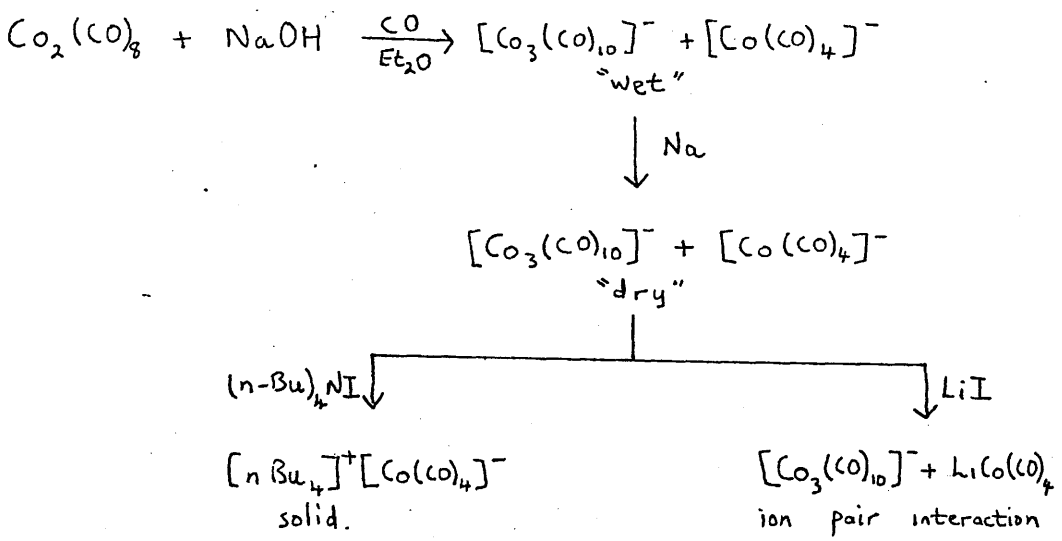


Figure 3.21.

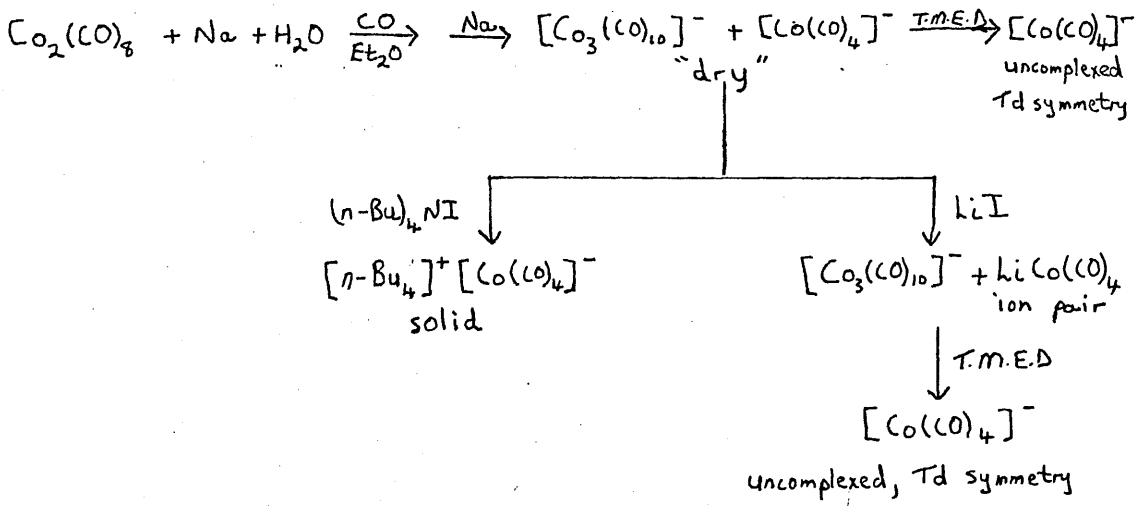


Figure 3.22.

CHAPTER 4

MERCURY - COBALT CARBONYL COMPOUNDS

CHAPTER 4 - MERCURY - COBALT CARBONYL COMPOUNDS

1. INTRODUCTION

The simplest and most common mercury - cobalt carbonyl compound is bis (tetracarbonyl cobalt) mercury, $Hg[Co(CO)_4]_2$. Its first appearance was reported by none other than W. Hieber and H. Schulten[60], when an aqueous solution of $HgCl_2$ was added to $HCo(CO)_4$ to precipitate the water insoluble $Hg[Co(CO)_4]_2$. Later this extremely stable derivative which is readily soluble in organic solvents was established to form quantitatively according to [142] :

$$HgX_2 + 3Co + 8CO \xrightarrow[200\ atm]{150^oC} Hg[Co(CO)_4]_2 + CoX_2,\ X = Br,\ I \qquad (4.1)$$

A more convenient "wet" method was described, which involved metathesis of a solution of $[Co(CO)_4]^-$ with a derivative of mercury e.g. an aqueous solution of the anion will react with mercury (II) cyanide to give the desired product[260]. Around the same time Behrens prepared the compound using a hydrocarbon solution of $[Co(CO)_4]_2$ with sodium amalgam[261]. More recently an elaborate synthesis of $Hg[Co(CO)_4]_2$ was described[262]. This involved the preparation of $KCo(CO)_4$ in a carbon monoxide atmosphere using cobaltous chloride hexahydrate, potassium hydroxide and potassium cyanide in water over a period of 24 to 72 hours. The mercury salt is made by adding mercuric (II) chloride and nitric acid to the $KCo(CO)_4$ solution, the crude product being filtered and purified by recrystallisation from acetone, a yield of 55 - 65% being achieved (the yield of the crude product being estimated at 85%). Metallic mercury will insert into $Co_2(CO)_8$ to give $Hg[Co(CO)_4]_2$[157].

The molecular crystal structure of this orange compound has been determined[263]. It was found to have approximately D_{3d} symmetry, its carbonyl groups staggered w.r.t. one another. Coordination about the

cobalt atoms is ideally trigonal bipyramidal but the equatorial carbonyls are bent towards the mercury atom. The Co - CO groups all appear to be linear. The $HgCo_2$ unit itself is linear and symmetrical, the mercury atom being within bonding distance of the two cobalts (see Fig. 4.1).

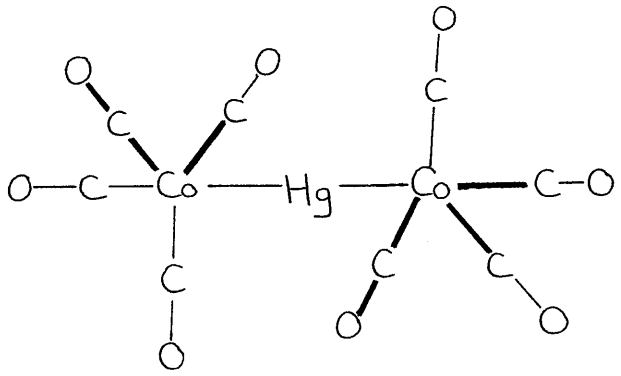


Figure 4.1

This molecular structure would have six fundamental stretching modes, three of them i.r. active ($2a_{2u} + e_u$) and three Raman active ($2a_{1g} + e_g$)[264].

In the carbonyl stretching region, good agreement was found between experimental i.r. and calculated i.r. values for a D_{3d} structure. Another i.r. study was conducted by Bor[265] using a ^{13}CO enriched species, which was prepared indirectly by enriching $Co_2(CO)_8$ with ^{13}CO then reacting this with metallic mercury to give $Hg[Co(CO)_4]_2$ - the product itself being very stable and so reluctant to undergo CO exchange. The observed carbonyl stretches, in hexane, are given in Table 4.1, confirming D_{3d} symmetry.

TABLE 4.1

Assigned		Raman	i.r.
a_{1g}	$\bar{\nu}_1(CO)$	2094.6	
	$\bar{\nu}_2(CO)$	2027.5	
a_{2u}	$\bar{\nu}_3(CO)$		2072.3
	$\bar{\nu}_4(CO)$		2021.7
e_g	$\bar{\nu}_5(CO)$	1996.0	
e_u	$\bar{\nu}_6(CO)$		2007.3

The isotopic studies also showed that the axial C - O stretching force constant is higher than the equatorial (radial), as in $HCo(CO)_4$ and $MeCo(CO)_4$.

The metal - metal stretching frequencies were also investigated. For $Hg[Co(CO)_4]_2$ these frequencies were $\bar{\nu}_1$ 161 cm^{-1} (Raman active) and $\bar{\nu}_3$ 196 cm^{-1} (i.r. active)[266], the former being the symmetric Hg - Co_2 stretch and the latter the asymmetric stretch.

To round off spectroscopic studies of $Hg[Co(CO)_4]_2$, the ^{59}Co n.m.r. spectrum has been reported[267].

To aid in the assignment of i.r. absorptions a series of derivatives of $Hg[Co(CO)_4]_2$ have been prepared and characterised[268]. These included secondary and tertiary phosphine, tertiary arsine and tertiary stibine complexes of the general formula $Hg[Co(CO)_3L]_2$. All were found to be yellow, air stable, crystalline solids except L = $P(n\text{-octyl})_3$ which is a liquid that decomposed slowly in air. Donor or chlorinated solvents tended to attack these compounds to give rapid decomposition. The i.r. absorbing regions were again 350 - 700 cm^{-1} and 1910 - 2100 cm^{-1}, due to Co - C - O vibrations. The ligand L was determined to be axially coordinated in a molecule of D_{3d} symmetry.

Preparation of $Hg[Co(CO)_3(siphos)_2]$, siphos = tris (trimethylsilyl-methyl) phosphine, by treating $[Co(CO)_3(siphos)]^-$ with mercury (II) cyanide or reacting $Hg[Co(CO)_4]_2$ directly with siphos at room temperature, gave a compound whose solution and solid state i.r. spectrum are consistent with, but do not distinguish between D_{3h} and D_{3d} structures with linear $HgCo_2$ moieties[269].

Most substituted compounds of the type $Hg[Co(CO)_3L]_2$ can react further, e.g.

$$Hg[Co(CO)_3L]_2 + HgX_2 \rightleftharpoons 2XHgCo(CO)_3L, \quad X = \text{halide} \qquad (4.2)$$

These halide derivatives were synthesised, and their i.r. spectra published for the first time in 1967, by reacting HgX_2 (X = Cl, Br) and HgClR (R = alkyl radical) with $NaCo(CO)_4$ yielding $HgYCo(CO)_4$ (Y = Cl, Br or R)[270].

$Hg[Co(CO)_4]_2$ will also undergo reactions with bases, for example pyridine[154] (py = pyridine).

$$3Hg[Co(CO)_4]_2 + 12py \longrightarrow 3Hg + 2[Co(py)_6][Co(CO)_4]_2 + 8CO \qquad (4.3)$$

This contrasted with the reaction with trimethylphosphite, $P(OMe)_3$, which led to a covalent derivative rather than a salt[271].

$$Hg[Co(CO)_4]_2 + P(OMe)_3 \longrightarrow Hg + 2CO + [Co(CO)_3P(OMe)_3]_2 \qquad (4.4)$$

These reactions have been suggested as a basis for purification of mercury but the expense of $Co_2(CO)_8$ would not normally be justified.

A simple method of preparing $[Co(CO)_4]^-$ is reduction of $Co_2(CO)_8$ (see equation 4.5), the most convenient reducing agent being sodium amalgam

$$Co_2(CO)_8 + 2e^- \longrightarrow 2[Co(CO)_4]^- ; \quad E^o = +0.4V^{272} \qquad (4.5)$$

However several instances have been reported where contamination of the anion by mercury containing compounds occurred. The best method of being rid of such impurities from other cobalt compounds is fractional sublimation[159] (the impurities in this example being caused by a 1% sodium amalgam in T.H.F.). A similar side reaction occurred using $Co_2(CO)_8$ and dilute sodium amalgam in hexane[157] where the mercury

compound was an intermediate stage. This sequence of reactions was also noted in diethyl ether although in both situations the reaction went to completion with $NaCo(CO)_4$ being isolated. This end product was also obtained from $Hg[Co(CO)_4]_2$ and sodium amalgam in diethyl ether. Reaction of supposed $NaCo(CO)_4$, prepared by reduction using sodium amalgam in T.H.F., with trimethylcyclopropenyl tetrafluoroborate gave $Hg[Co(CO)_4]_2$ and $Me_3C_3COCo(CO)_3$ as the two carbonyl containing products of reaction[273].

The reactions of $Hg[Co(CO)_4]_2$ with halides, amines and organometallic Lewis bases has been very adequately described[274]. $[Co(CO)_4]^-$ will react with $Hg[Co(CO)_4]_2$ to give the anionic species $\{Hg[Co(CO)_4]_3\}^-$ (see later). Lewis bases e.g. 2,2' - bipyridyl and 1,10-phenanthroline react giving yellow crystalline complexes $(L - L)Hg[Co(CO)_4]_2$ where L - L is a bidentate ligand. These complexes tend to dissociate in solution according to:

$$(L - L)Hg[Co(CO)_4]_2 \rightleftharpoons L - L + Hg[Co(CO)_4]_2 \qquad (4.6)$$

because bidentate ligands are poor Lewis bases w.r.t. mercury.

They will decompose on standing under nitrogen,

$$6(L - L)Hg[Co(CO)_4]_2 \longrightarrow 3Hg + 8CO + 2[Co(L - L)_3]^{2+} + [Co(CO)_4]^- + 3\{Hg[Co(CO)_4]_3\}^- \qquad (4.7)$$

Using LiX and $Hg[Co(CO)_4]_2$ in T.H.F. will give anions of the type $\{XHg[Co(CO)_4]_2\}^-$, X = Br, I, Cl, which closely resemble $\{Hg[Co(CO)_4]_3\}^-$ in i.r. spectra.

The anionic species $\{Hg[Co(CO)_4]_3\}^-$ carved a niche for itself in the late sixties. It was first recorded by Marko et al. as a reduced species caused by the action of sodium amalgam on $Hg[Co(CO)_4]_2$ (in a 1:1 ratio w.r.t. Na^+)[275]. At this time it was accorded the formula $\{Hg[Co(CO)_4]_2\}^-$, the counterion being $[Fe(\underline{o}phen)_3]^{2+}$ (using excess amalgam gave the boring anion $[Co(CO)_4]^-$). The compound was a deep

orange colour in solution ($Hg[Co(CO)_4]_2$ is yellow) and its i.r. spectrum had strong bands at 2035, and 1969 cm^{-1} which were similar to the strong absorptions of $Hg[Co(CO)_4]_2$ but shifted by 37 - 38 cm^{-1} to lower frequencies. The authors speculated that the reaction sequence was :

$$Hg[Co(CO)_4]_2 \xrightarrow{Na/Hg} \{Hg[Co(CO)_4]_2\}^- \xrightarrow[excess]{Na/Hg} 2[Co(CO)_4]^- + Hg \quad (4.8)$$

In its red solid form, this compound had a strong broad signal at 1960 cm^{-1} (as a K.Br disc). It was also made using $Hg[Co(CO)_4]_2$ and $[Co(CO)_4]^-$ in T.H.F., with air oxidation reversing the reaction. The near likeness of the i.r. spectra of the neutral and anionic mercury compounds suggested a linear arrangement of the three metal atoms, D_{3d} symmetry, with the mercury atom playing a significant role in the dispersion of negative charge (by comparison with the 37 - 54 cm^{-1} shift of $Co_4(CO)_{12}$ and $[FeCo_3(CO)_{12}]^-$ species).

Condemnation of the assignment of this species was not long in coming. Burlitch et al. led the way, commenting that although an intermediate species in the reaction of $Hg[Co(CO)_4]_2$ with sodium amalgam was not unreasonable, the reduction of $Hg[Co(CO)_4]_2$ to its anion by $[Co(CO)_4]^-$ was very unusual[276]. Using equimolar amounts of $Hg[Co(CO)_4]_2$ and $NaCo(CO)_4$ in T.H.F., under argon, a solution showing very strong i.r. signals at 2036 and 1986 - 58 (broad) cm^{-1} was prepared. There were also weak absorptions at 2068, 1895 sh and 1862 cm^{-1}, the first arising from unreacted $Hg[Co(CO)_4]_2$ and the latter two from $[Co(CO)_4]^-$ in T.H.F.[205]. However if $[Co(CO)_4]^-$ was acting as a reducing agent, $Co_2(CO)_8$ should be present as the oxidised species, see equation 4.9, and of this there was no trace.

$$Hg[Co(CO)_4]_2 + [Co(CO)_4]^- \longrightarrow \{Hg[Co(CO)_4]_2\}^- + Co(CO)_4 \downarrow \tfrac{1}{2}Co_2(CO)_8 \quad (4.9)$$

Evidence of the species being diamagnetic and exhibiting no e.s.r. signal led these people to believe that the actual composition of the anion was $\{Hg[Co(CO)_4]_3\}^-$. To lend further weight to their arguments, the crystal structure of $[Fe(\underline{o}phen)_3]\{Hg[Co(CO)_4]_3\}_2$ was determined. From the observed density and unit cell parameters, the molecule was calculated to have a molecular weight of 2038. For x = 2 and 3, $[Fe(\underline{o}phen)_3]\{Hg[Co(CO)_4]_x\}_2$ has molecular weights of 2023 and 1681 respectively. Analytical results for the reactions outlined in Fig. 4.2 are also consistent with a $Co(CO)_4$: Hg ratio of 3:1

$$\{Hg[Co(CO)_4]_3\}^- \longrightarrow Hg[Co(CO)_4]_2 + [Co(CO)_4]^-$$

$$\downarrow Ph_3P \qquad \downarrow \text{excess } [Ni(\underline{o}phen)_3]^{2+}$$

$$Hg[Co(CO)_3PPh_3]_2 \qquad \tfrac{1}{2}[Ni(\underline{o}phen)_3][Co(CO)_4]_2$$

Figure 4.2

The likely arrangement of the four metal atoms of the anion was thought to be planar, the carbonyl groups being staggered to give a molecule of C_{3v} symmetry. This would have seven i.r. active carbonyl stretching frequencies but as Bor had shown[265] coupling of the stretching vibrations of carbonyl ligands in different cobalt environments is quite small except for that of <u>trans</u> axial groups acting through a linear sequence of bonds. Since $\{Hg[Co(CO)_4]_3\}^-$ did not enjoy a linear arrangement of ligands, local symmetry (of C_{3v}) would give three i.r. active bands. Only two are observed, probably the missing absorption is hidden in the broad band which is a consequence of using polar solvents to dissolve the complex.

Another group also came out against Marko et al. They showed that $Hg[Co(CO)_4]_2$ and sodium always gave elemental mercury regardless of stoichiometry [277]. Again they pointed out that reduction of

$Hg[Co(CO)_4]_2$ by $[Co(CO)_4]^-$ should give the oxidised species $Co_2(CO)_8$. They found that solution spectra, magnetic data, elemental analysis and stoichiometry of the preparations indicated that the anion of $Hg[Co(CO)_4]_2$ is $\{Hg[Co(CO)_4]_3\}^-$, a complex anion of Hg(II). In solution it would exist in equilibrium with $[Co(CO)_4]^-$ and $Hg[Co(CO)_4]_2$ and will react with Ph_3P to precipitate $Hg[Co(CO)_3PPh_3]_2$, which is well characterised[271], from solution. In conclusion the reaction of $Hg[Co(CO)_4]_2$ and $[Co(CO)_4]^-$ is not reduction to an Hg(I) species but complexation to give an Hg(II) anion, analogous to other mercurate(II) complexes of type $[HgX_3]^-$, X = halide[278]. The reaction sequence is:

$$Hg[Co(CO)_4]_2 + 2Na \longrightarrow 2NaCo(CO)_4 + Hg$$

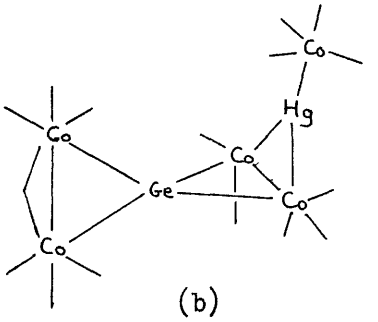
$$NaCo(CO)_4 + Hg[Co(CO)_4]_2 \longrightarrow Na\{Hg[Co(CO)_4]_3\} \xrightarrow{2Na} 3NaCo(CO)_4 + Hg$$

Figure 4.3

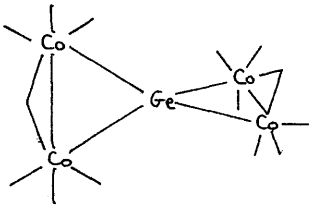
This mercury anionic species reacts with halides (e.g. $[Ph_3PCH_2Ph]^+X^-$, X = Cl,I) displacing $[Co(CO)_4]^-$ to give $[Ph_3PCH_2Ph]^+\{XHg[Co(CO)_4]_2\}^-$ which has the i.r. absorptions 2052m and 1983vs cm^{-1} in addition to a weak signal at 2070 cm^{-1}, due to $Hg[Co(CO)_4]_2$[275]. The shift to lower frequency indicates that the $Co(CO)_4$ groups bear a fractional negative charge.

As shown earlier[275] Lewis base derivatives of $Hg[Co(CO)_4]_2$ (i.e. L - L $Hg[Co(CO)_4]_2$) will decompose to give $\{Hg[Co(CO)_4]_3\}^-$, and X^- (X = Cl, Br or I) can replace one $[Co(CO)_4]^-$ moiety in the complex, although further reaction to give $\{Br_2Hg[Co(CO)_4]_2\}^{2-}$ could not be achieved. The decomposition of $\{XHg[Co(CO)_4]_2\}^-$ to $[Co(CO)_4]^-$ is both solvent and halide dependent; this will not occur in dichloromethane or chloroform and in T.H.F. or D.M.F. only a very weak signal for $[Co(CO)_4]^-$ is observed. The concentration of $[Co(CO)_4]^-$ increases in the order Cl < Br < I although it is very small in all cases.

Compounds containing the $HgCo(CO)_4$ species have been made using germanium - cobalt carbonyl species leading to formation of $[NEt_4]^+ [Ge\{Co_2(CO)_7\}\{Co_2(CO)_6[HgCo(CO)_4]\}]^-$ which contains a mercury bridged Co - Co bond[279]. The reaction of $[Co(CO)_4]^-$ or $Co_2(CO)_8$ with GeI_4 to give $Ge\{Co_2(CO)_7\}_2$ was being investigated using sodium amalgam to reduce $Co_2(CO)_8$ in T.H.F.[280]. (The crystal structure of this compound is shown in Fig. 4.4a). Of course under such conditions mercury containing species are formed and this proved no exception. Since chemical and spectroscopic techniques could not convincingly characterise this newcomer XRay crystallography was employed and the structure is shown in Fig. 4.4b. It is <u>formally</u> derived by replacing one μCO group of the simple Ge - Co species by a hypothetical $\mu[HgCo(CO)_4]^-$ group to give this first example of a mercury bridged Co - Co bond.



(b)



(a)

Figure 4.4

The overall reaction is:

$$GeI_4 + 5\,[Co(CO)_4]^- + Hg \longrightarrow [HgGeCo_5(CO)_{17}]^- + 4I^- + 3CO \quad (4.10)$$

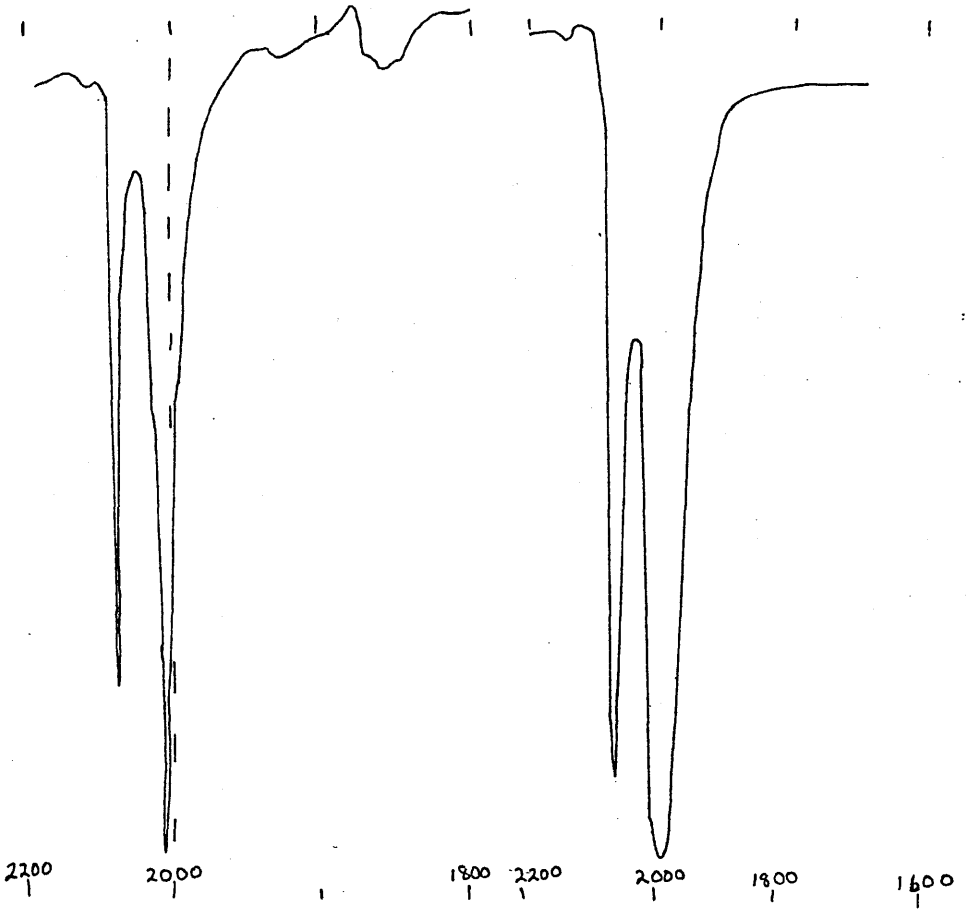
although the detailed pathway is still obscure. The authors found that if great care was taken to separate the $[Co(CO)_4]^-$ containing solution from the amalgam, a different anionic product with a similar i.r. spectrum could be obtained which did not contain mercury ($\nu(CO)$ $[CH_2Cl_2]$: 2078w, 2048w, 2022vs, 1995w and 1968 br cm^{-1}). This reaction is unusual because mercury usually inserts into such M - M bonds, not bridge them. Perhaps this bridging is the first step of mercury insertion reactions which is stopped at this stage here because complete insertion would necessitate the breakdown of the $GeCo_2$ unit.

In the rest of this chapter, work involving the preparation of Hg - Co containing complexes including the $\{Hg[Co(CO)_4]_3\}^-$ anion, and their isolation will be discussed.

2. REACTIONS OF $Hg[Co(CO)_4]_2$ IN ETHEREAL SOLVENTS.

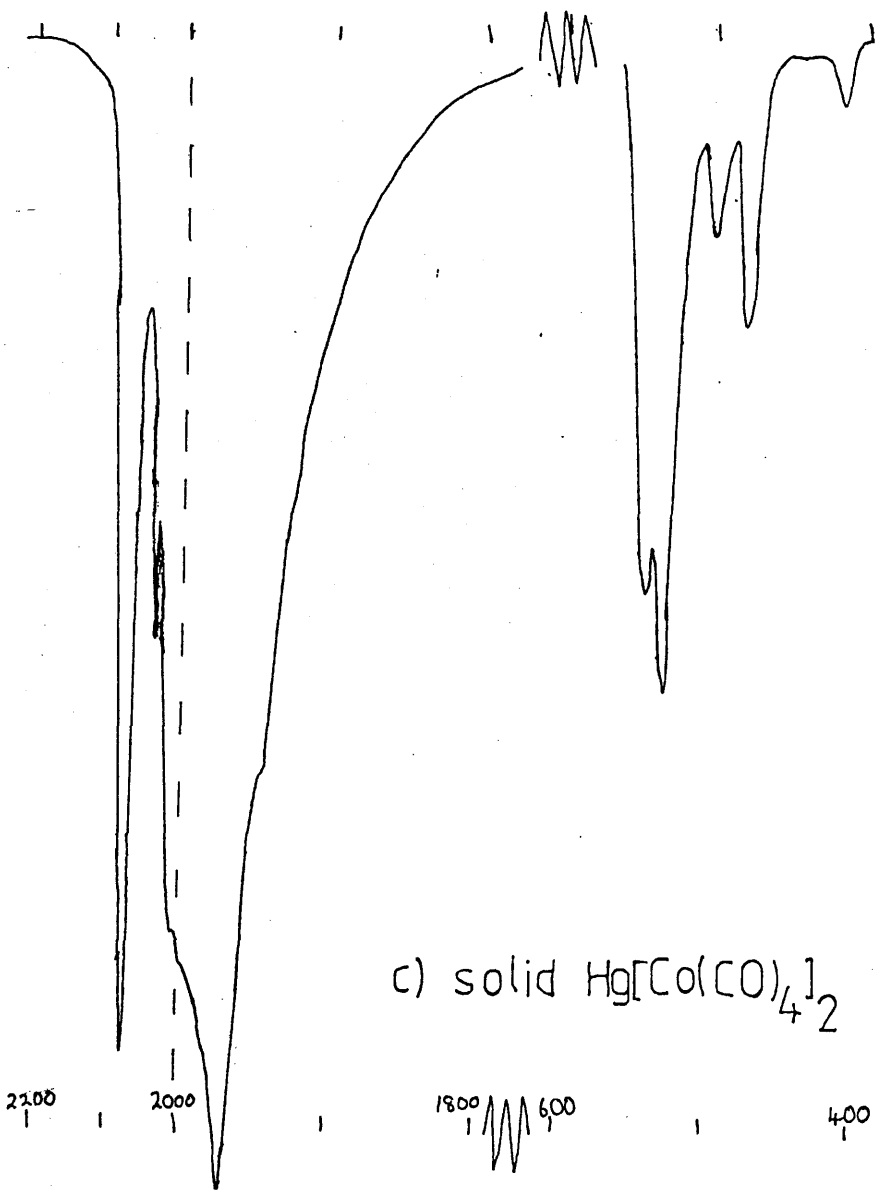
To explore the possibility of using $[Fe(o\text{phen})_3]^{2+}$ to isolate cobalt carbonyl anions, the experiments of Marko et al.[275] and Burlitch et al.[276] were repeated under both carbon monoxide and nitrogen. $Hg[Co(CO)_4]_2$ was prepared and isolated following their instructions and its purity established by its i.r. spectrum, under various solvent conditions, and its visible / U.V. spectrum of the solid (Fig. 4.5).

The yellow compound was then dissolved in T.H.F., under nitrogen, with some sodium amalgam present, and stirred. To isolate the product, $Fe(o\text{phen})_3Cl_2$ (as an aqueous solution) was added and a red precipitate obtained; the solution and solid i.r. spectrum of the product is shown in Fig. 4.6



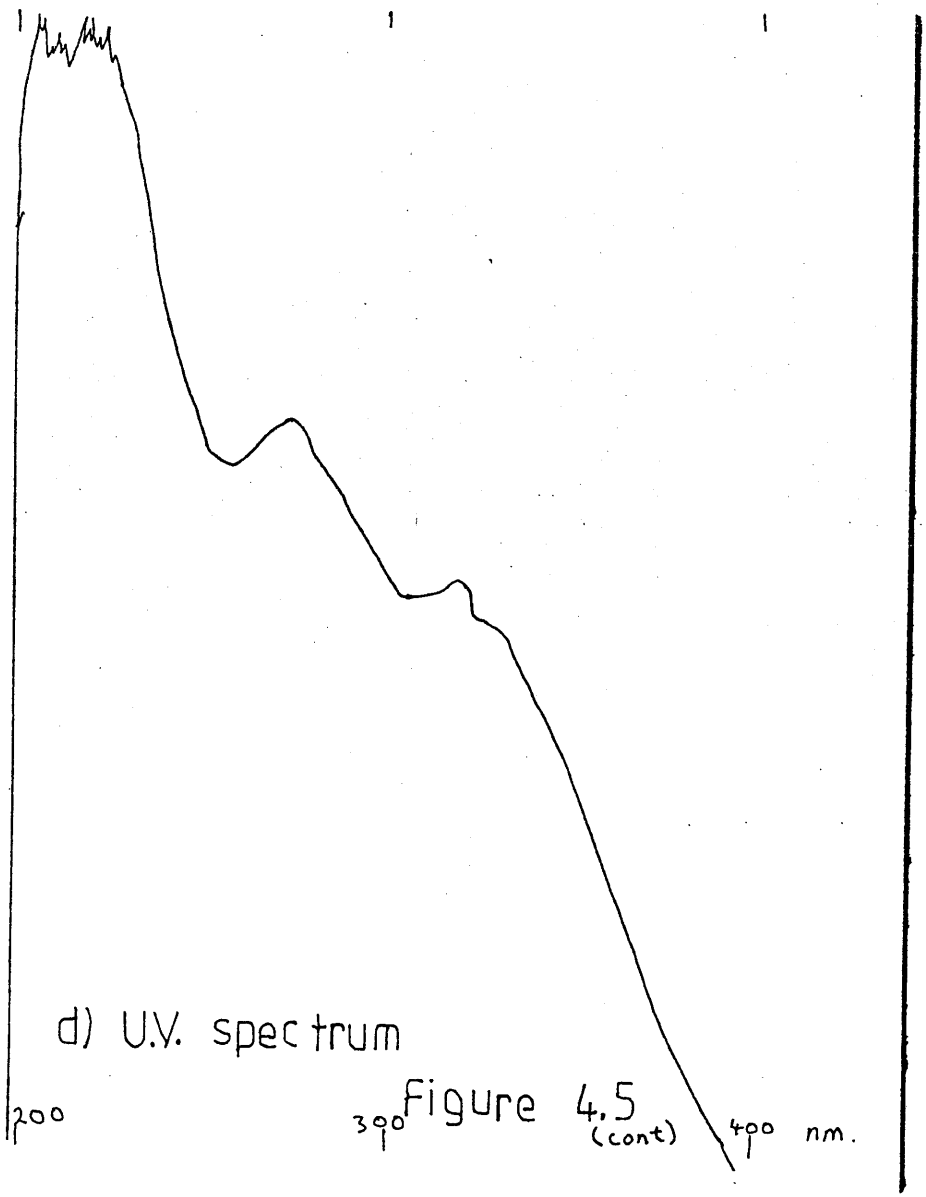
a) $Hg[Co(CO)_4]_2$ in hexane

b) in T.H.F.



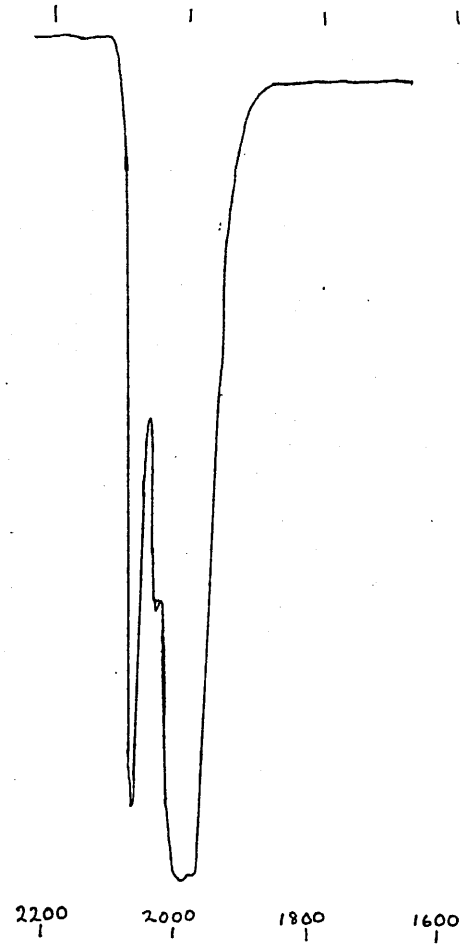
c) solid $Hg[Co(CO)_4]_2$

Figure 4.5



d) U.V. spectrum

Figure 4.5 (cont)



a) after 3hrs

Figure 4.6

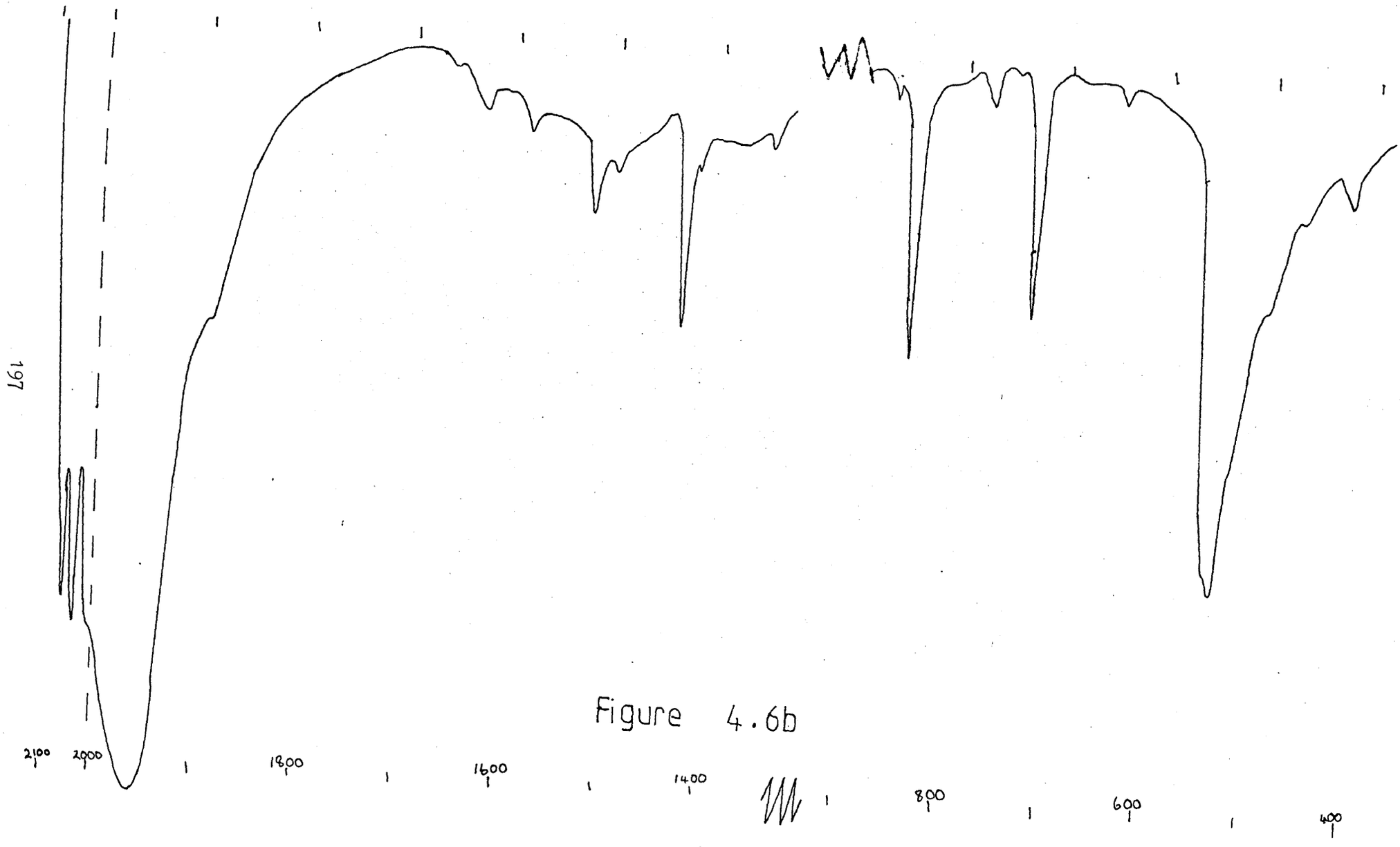


Figure 4.6b

By comparison with earlier work[275,276], the signals in the solid i.r. spectrum at 2040 and 1965 cm^{-1} are of the anion $\{Hg[Co(CO)_4]_3\}^-$. Burlitch assigned the signal at 2068 cm^{-1}, in his work, tentatively to $Hg[Co(CO)_4]_2$; in the present work it was found that the higher frequency signal was at 2060 cm^{-1} and did not correspond closely to the solid i.r. spectrum of $Hg[Co(CO)_4]_2$. This has been cautiously assigned to a new species in the reaction - $\{XHg[Co(CO)_4]_2\}^-$, X = Cl or Br depending on which halides are present in solution. These complexes are known and their i.r. spectra in T.H.F. reported as follows:[274] X = Cl - 2075w, 2051s, 1979vs, 1896vw; X = Br - 2071w, 2048s, 1979vs, 1896vw. The signals at 1896 cm^{-1} are due to $[Co(CO)_4]^-$, that around 2070 cm^{-1} is too weak to be observed in this example and the signal at 1979 cm^{-1} appears as a shoulder, at slightly higher frequency, of the main $\{Hg[Co(CO)_4]_3\}^-$ signal. During the work up a solid was deposited on the sides of the reaction flask which apparently consisted entirely of the new compound (Fig. 4.7a). The aqueous layer also surrendered a solid compound whose i.r. spectrum was identical to that of $[Co_3(CO)_{10}]^-$ (Fig. 4.7b).

Repetition of the experiment gave similar results, only the ratio of the mercury containing anions being slightly altered.

Using $Ni(\underline{o}phen)_3Cl_2$, instead of the iron analogue, again gave both mercury containing anionic species along with an extra product which would appear to be $[Ni(\underline{o}phen)_3]^{2+}[Co(CO)_4]_2^-$, the simple cobalt anion compound.

Repeating this work in diethyl ether gave a similar reddish solid whose i.r. spectrum showed both $Hg[Co(CO)_4]_2$ and $\{Hg[Co(CO)_4]_3\}^-$ to be present.

Allyl bromide ($CH_3 - CH = CHBr$) was added to $Hg[Co(CO)_4]_2$ in T.H.F. but the i.r. spectrum did not change from that of $Hg[Co(CO)_4]_2$ in

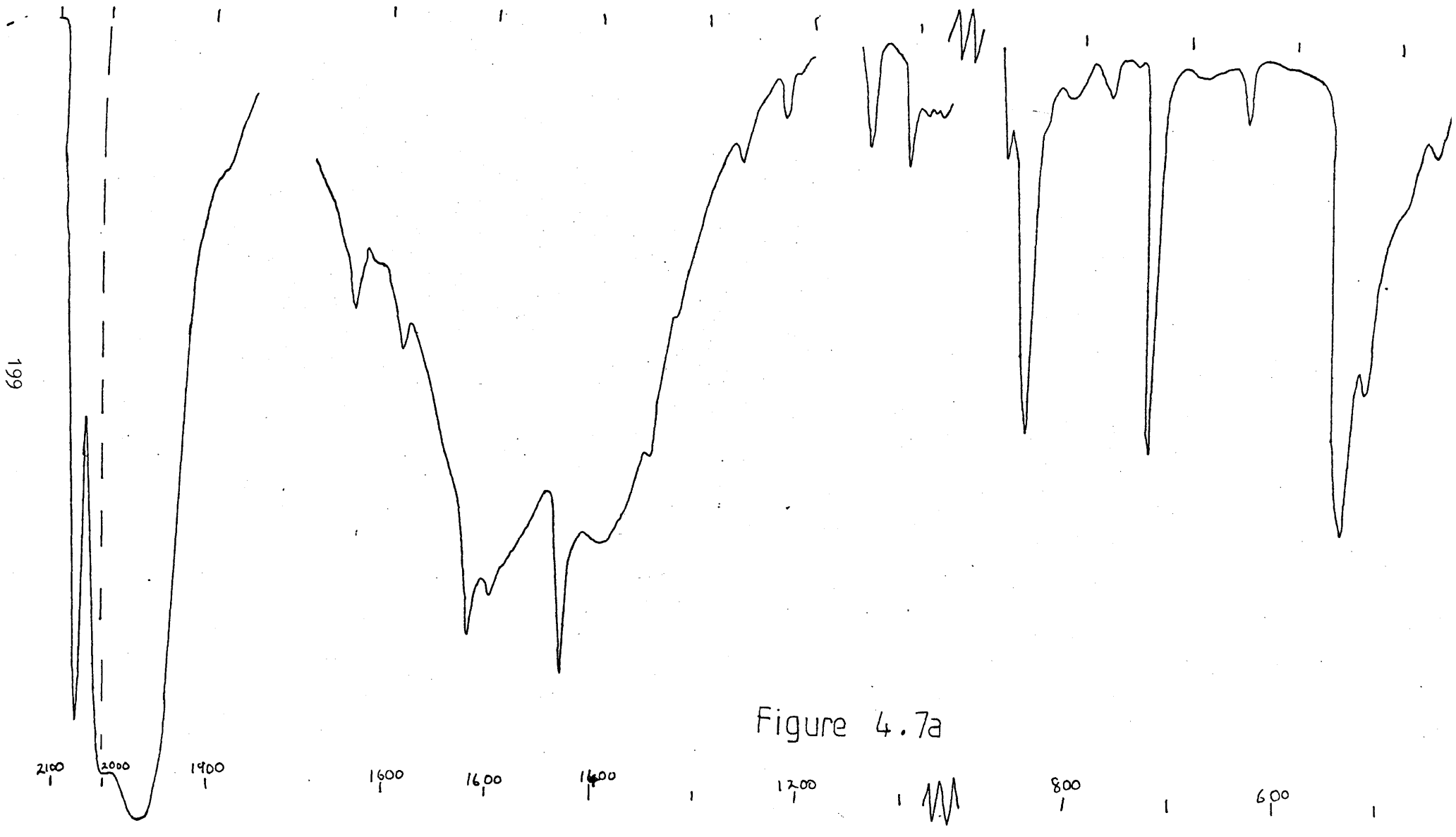


Figure 4.7a

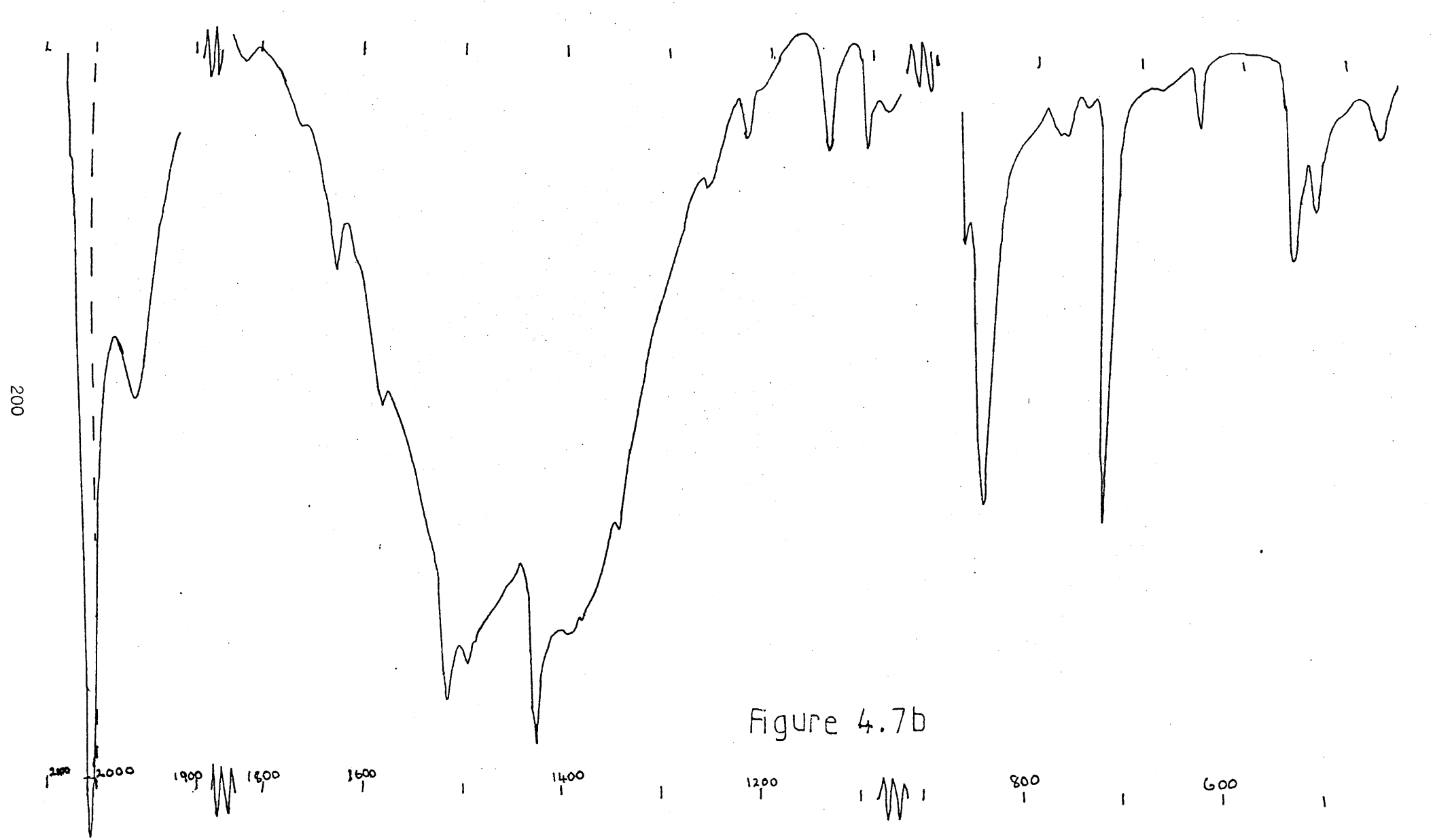


Figure 4.7b

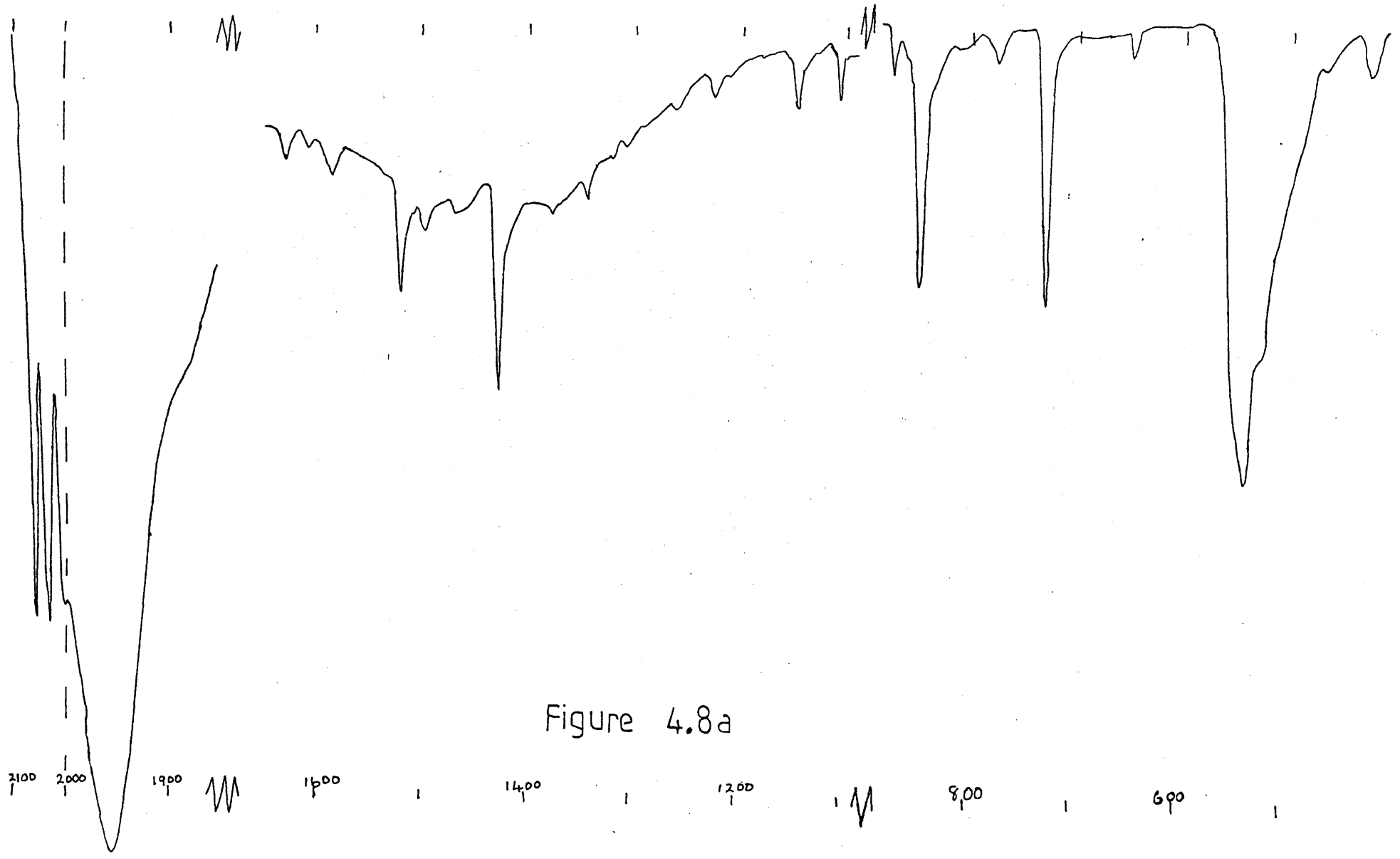


Figure 4.8a

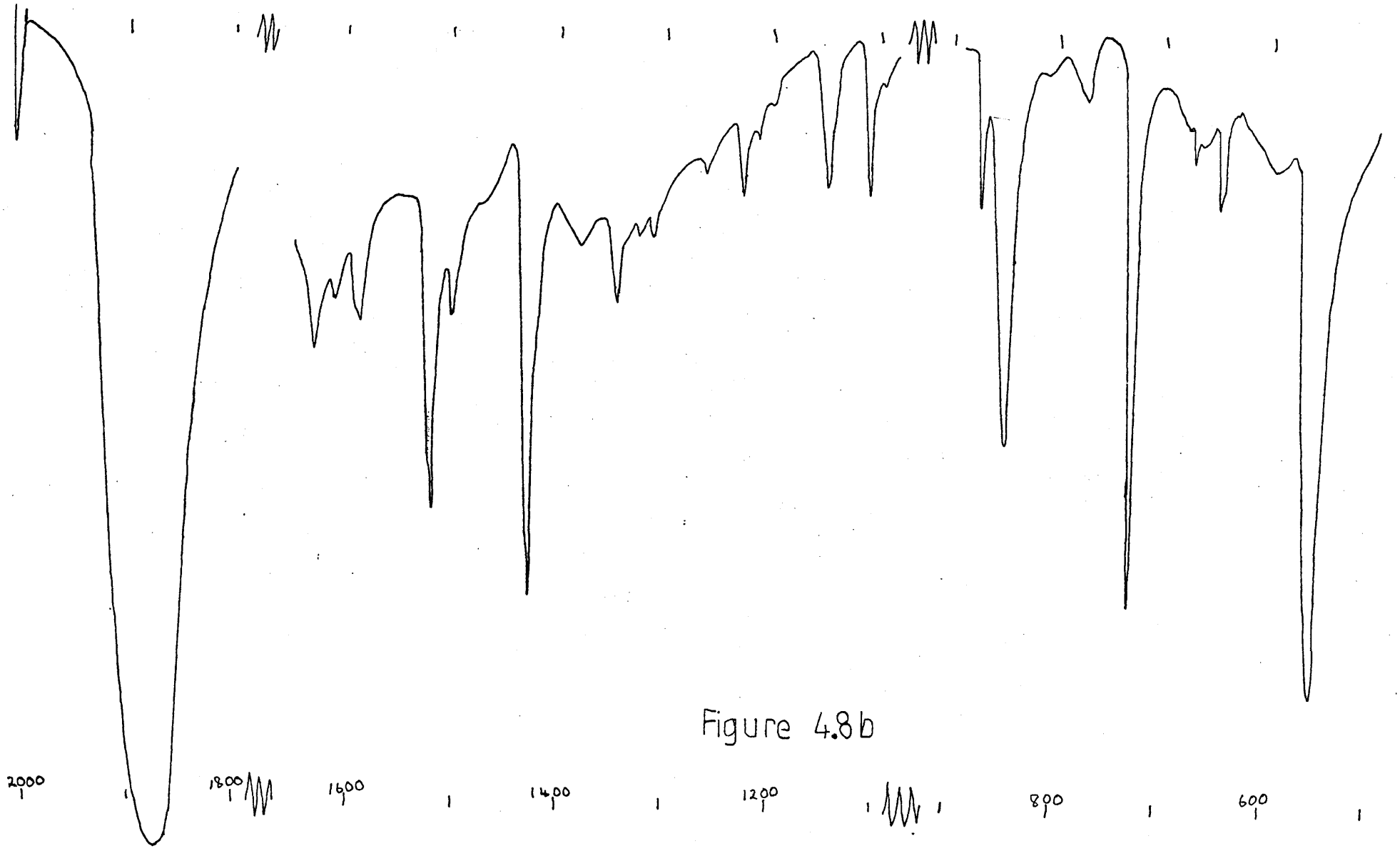


Figure 4.8b

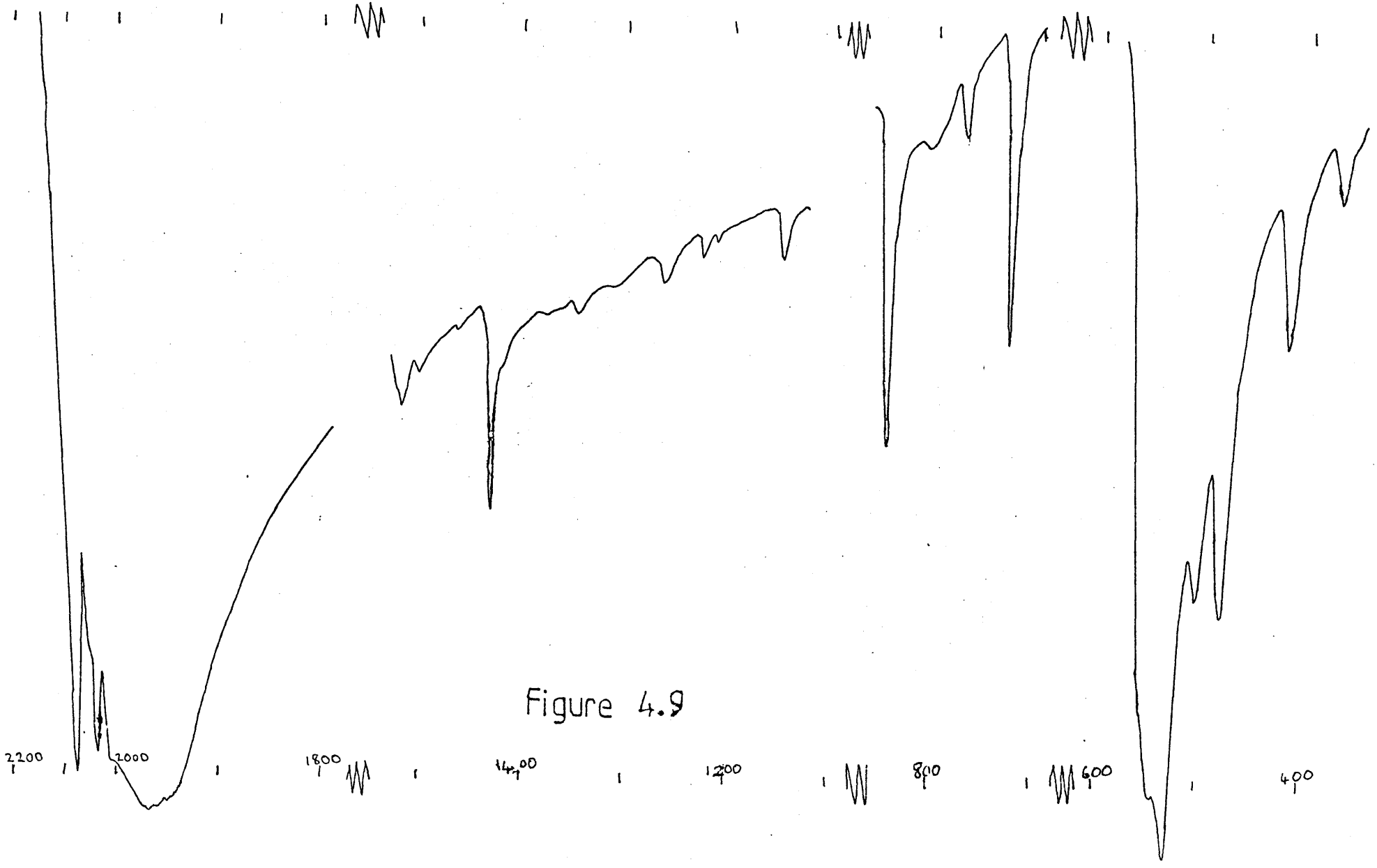


Figure 4.9

five days. This was verified by running expanded spectra of the reaction solution and of $Hg[Co(CO)_4]_2$ in T.H.F. since the i.r. bands for allylcobalt tricarbonyl and $Hg[Co(CO)_4]_2$ are very close.

3. REACTIONS OF $Co_2(CO)_8$ WITH SODIUM AMALGAM OR MERCURY IN ETHEREAL SOLVENTS

In a bid to reduce $Co_2(CO)_8$ to $[Co(CO)_4]^-$ in diethyl ether, sodium amalgam was added, under carbon monoxide. This quickly proved capable of producing the most complicated i.r. spectrum yet. After three hours evidence of $[Co_3(CO)_{10}]^-$ with some $Co_2(CO)_8$ was obtained. (Fig. 4.10a). Three hours later $[Co(CO)_4]^-$ was present with some $\{Hg[Co(CO)_4]_3\}^-$ (Fig. 4.10b) and after thirty hours, the i.r. spectrum of Fig. 4.10c was obtained. On standing for several days the only noticeable change was that of the intensities of certain signals (Fig. 4.10d). Addition of a few drops of water only altered the i.r. spectrum very slightly. In an effort to assign i.r. signals to species in solution, a plot of $\log (I_o/I)$ versus time was constructed which showed various species present at different times in the reaction, including $Co_2(CO)_8$ (signals at 2070, 2060 and 1865 cm^{-1}), $[Co_3(CO)_{10}]^-$ (signals at 2010 and 1995 cm^{-1}), $\{Hg[Co(CO)_4]_3\}^-$ (signals at 2035 and 1965 cm^{-1}) and $[Co(CO)_4]^-$ (signals at 1905, 1835 and 2010 - A_1 mode, cm^{-1}). A plausible reaction sequence is outlined in Fig. 4.11.

$Co_2(CO)_8$ + Na/Hg

↓

$Co_2(CO)_8 + [Co_3(CO)_{10}]^-$ + a little $\{Hg[Co(CO)_4]_3\}^-$

↓

$\{Hg[Co(CO)_4]_3\}^-$ + a little $[Co(CO)_4]^-$ and $[Co_3(CO)_{10}]^-$

↓

$[Co(CO)_4]^-$ + $\{Hg[Co(CO)_4]_3\}^-$

↓ air oxidation?

$[Co(CO)_4]^-$ + $[Co_3(CO)_{10}]^-$ + unidentified species + a little $\{Hg[Co(CO)_4]_3\}^-$

Figure 4.11

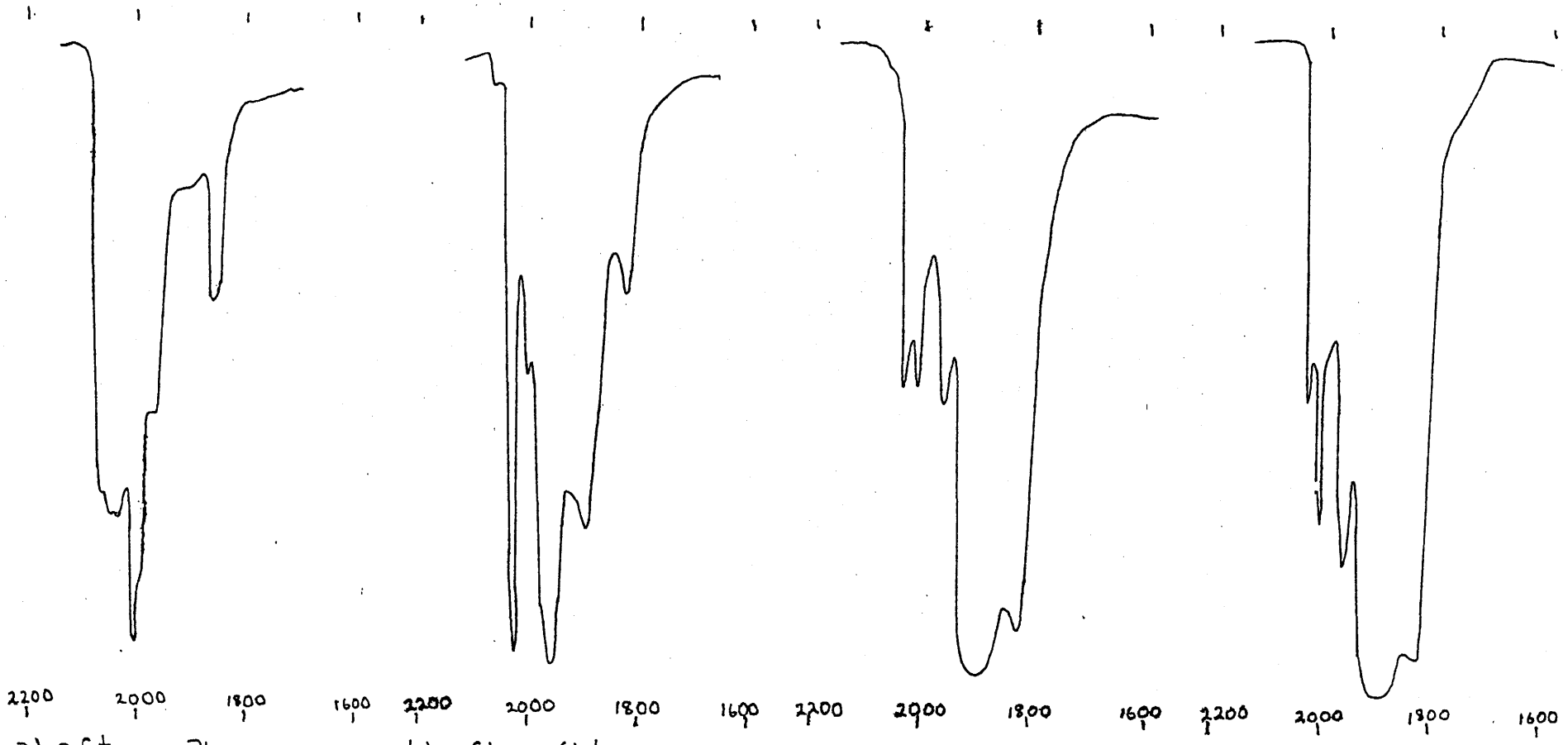
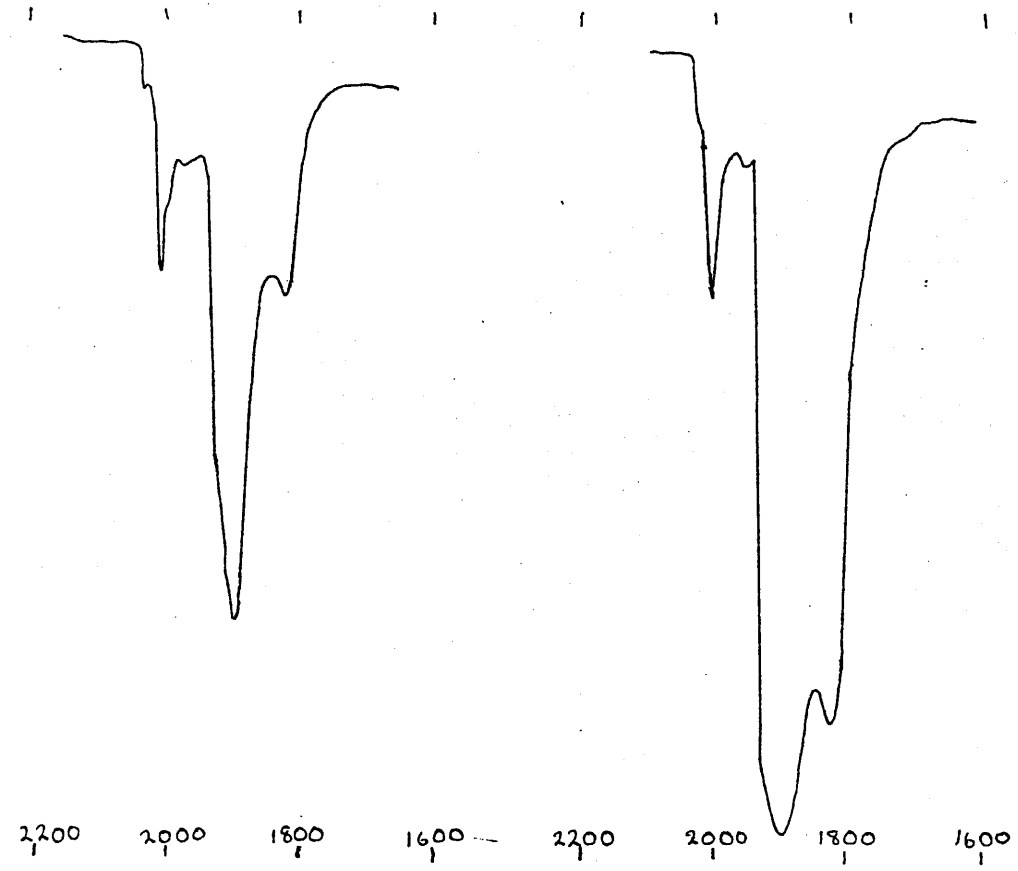

2200
2000
1800
1600
a) after 3hrs
b) after 6½hrs
c) after 30hrs
d) after 3days

Figure 4.10

It is thought that $\{Hg[Co(CO)_4]_3\}^-$ and $[Co(CO)_4]^-$ are present to some extent along with an unidentified species. ($\{Hg[Co(CO)_4]_2X\}^-$ cannot be present since there is no halide in solution). Assignment is made difficult by the high concentrations of cobalt carbonyl species present leading to too intense an i.r. spectrum. The broad, very strong signals at 1900 and 1830 cm^{-1} are reminiscent of the $[Co(CO)_4]^-$ signal and its side band in dry diethyl ether, when perturbed by Na^+ (see chapter 3), with $[Co_3(CO)_{10}]^-$ being present earlier in the reaction (c.f. Fig. 4.10a). Addition of a few drops of water led to loss of the signal at 1835 cm^{-1}, i.e. we now have wet anion, but did not affect the signals of the unknown species.

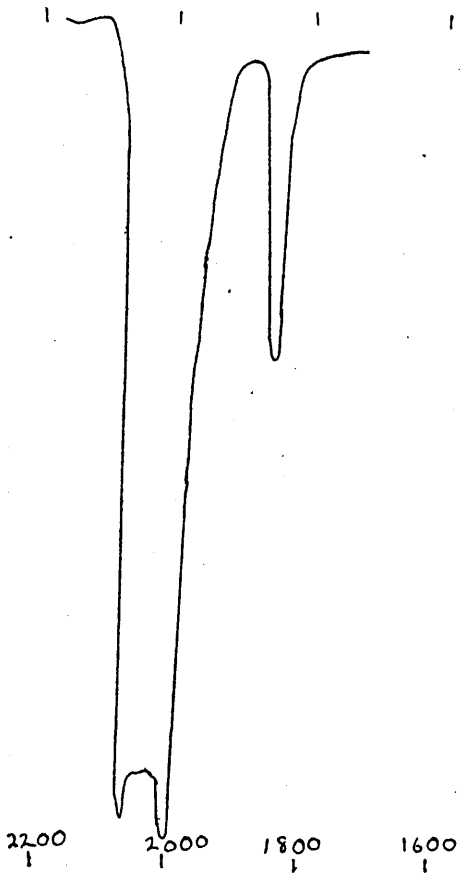
If the work is repeated in wet diethyl ether, under carbon monoxide, $[Co(CO)_4]^-$ is formed with $[Co_3(CO)_{10}]^-$ present at the intermediate stage, as already seen. Addition of LiBr to the solution containing only $[Co(CO)_4]^-$ (Fig. 4.12a) leads to a slight change in the equilibrium with a little $[Co_3(CO)_{10}]^-$ creeping back into solution (Fig. 4.12b). To identify if the complications were occurring because of the presence of mercury or because of Na^+, reactions of $Co_2(CO)_8$ in diethyl ether and under carbon monoxide were undertaken, adding mercury initially, then LiBr. A mixture of $Co_2(CO)_8$ and $Hg[Co(CO)_4]_2$ was found to be present after five hours (Fig. 4.13a). Addition of LiBr at this stage gave an orange / brown solution after ten minutes (from a dark brown colour) and the i.r. spectrum of Fig. 4.13b was obtained - this was previously assigned to $\{Hg[Co(CO)_4]_3\}^-$ but the possibility of $\{Hg[Co(CO)_4]_2Br\}^-$ cannot be ruled out. Removal of mercury from solution and leaving it overnight did not alter the spectrum but a further day of stirring, under carbon monoxide, gave a mixture of $\{Hg[Co(CO)_4]_3\}^-$ (?) and $Hg[Co(CO)_4]_2$ (Fig. 4.13c) the latter growing in strength as time went on.



a) after 19hrs

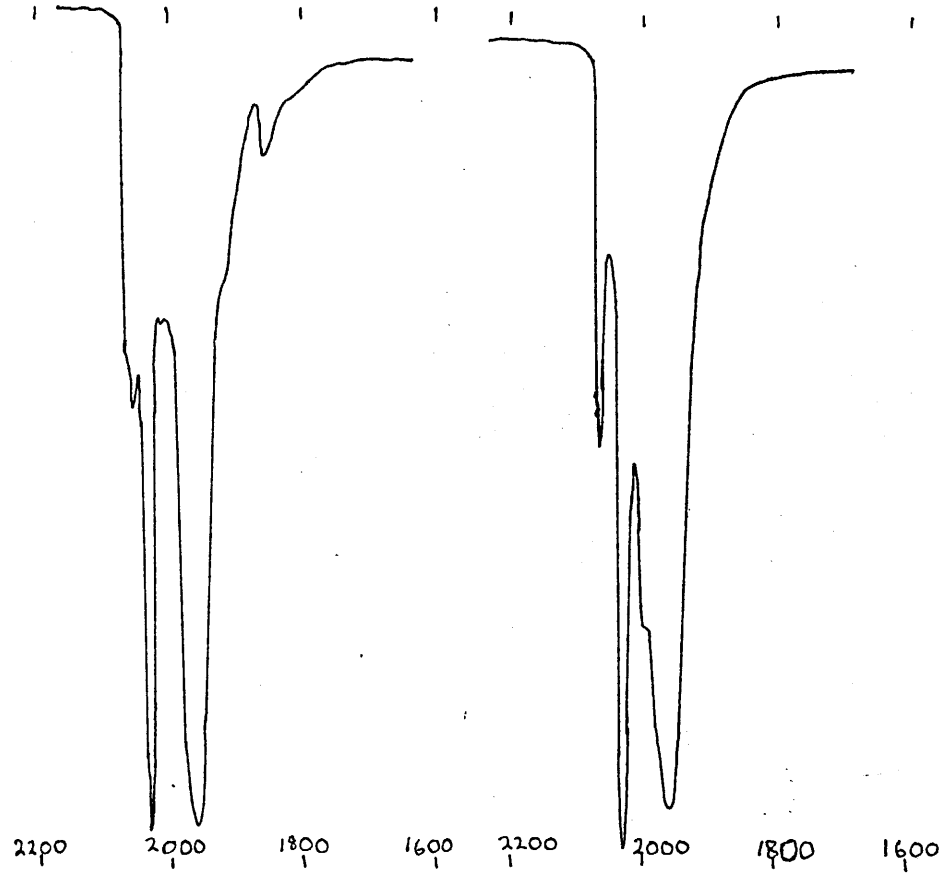
b) after 24 hrs; Li Br added

Figure 4.12



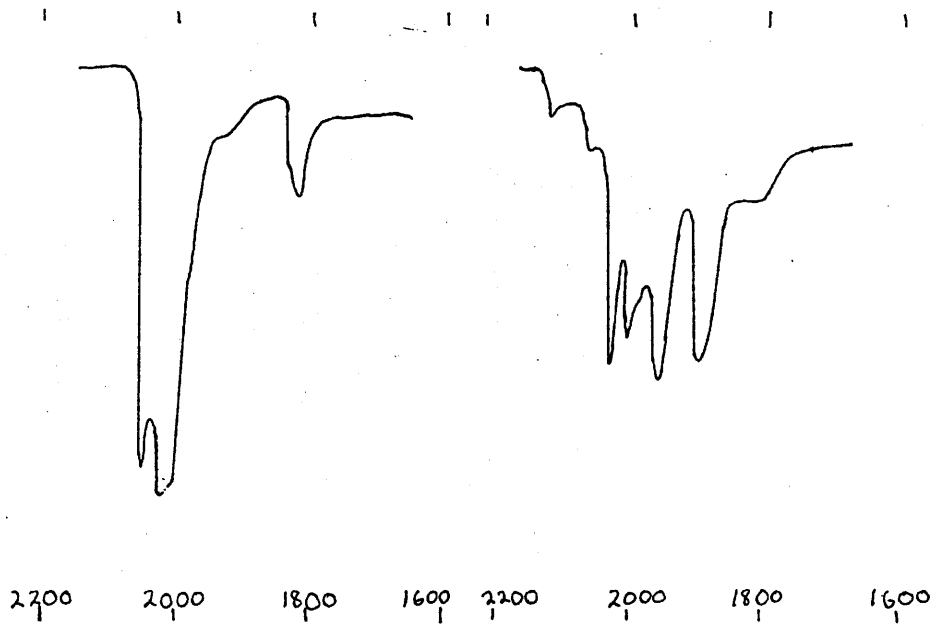
a) after 4½ hrs

Figure 4.13



b) after 10 mins c) after 24 hrs

Figure 4.13 [cont.- see text]



a) after 3 hrs b) 100 mins after Li Br added

Figure 4.14 [see text]

If LiBr is added before the mercury had interacted with $Co_2(CO)_8$ to any noticeable degree, formation of $[Co_3(CO)_{10}]^-$ and $[Co(CO)_4]^-$ plus some mercury containing complexes is found (see Fig. 4.14a & b).

If $Fe(\underline{o}phen)_3Cl_2$ is added to a solution containing such species, the solid isolated is of the simple anion $[Co(CO)_4]^-$ (Fig. 4.14c), the very sharp signal at $2005cm^{-1}$ being the symmetric A_1 mode of the undistorted tetrahedral anion. Some impure $Hg[Co(CO)_4]_2$ was also isolated.

Turning our attention to similar work in T.H.F., a mixture of $Co_2(CO)_8$, mercury and LiBr were stirred for three hours under carbon monoxide and the products isolated, as the $[Fe(\underline{o}phen)_3]^{2+}$ salts, were a mixture of $[Co(CO)_4]^-$ and $\{Hg[Co(CO)_4]_2X\}^-$, X = Cl and Br (see Fig. 4.15a). Extra mercury, more active stirring and a drier solid product (w.r.t. water content of the solid) enable $\{Hg[Co(CO)_4]_3\}^-$ to be the major product (Fig. 4.15b) with some $\{Hg[Co(CO)_4]_2X\}^-$ present.

Repeating the work and using $[Ni(\underline{o}phen)_3]^{2+}$ as the counterion gave a mixture of products - $[Co(CO)_4]^-$, $\{Hg[Co(CO)_4]_3\}^-$, $\{Hg[Co(CO)_4]_2X\}^-$ and $Hg[Co(CO)_4]_2$ all being isolated at various stages of the work up (see Fig. 4.16).

Again X could be both Cl and Br.

4. EXPERIMENTAL

1) Preparation of $Hg[Co(CO)_4]_2$

Following in the footsteps of Marko et al.[275], 6.10g $Co_2(CO)_8$ [17.85×10^{-3} moles] was dissolved in 150 ml methanol, under nitrogen, to form a dark brown solution, becoming pink over the next two hours. This was filtered into 150 ml aqueous solution of $HgCl_2$ [3.30g, 12.16×10^{-3} moles]. This was stirred for ten minutes to enable the original yellow and brown layers to intermingle and give a yellow / orange solution.

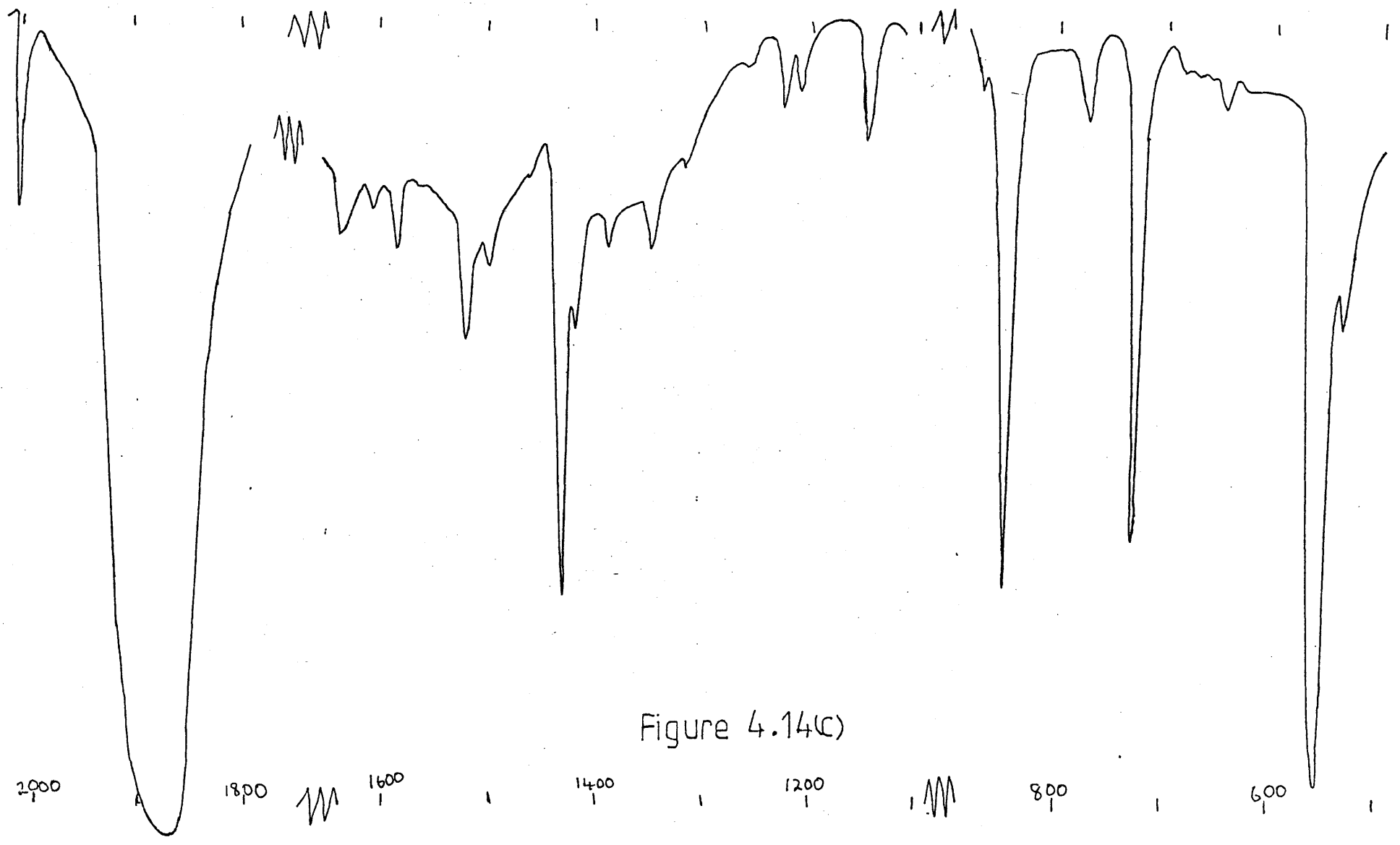


Figure 4.14(c)

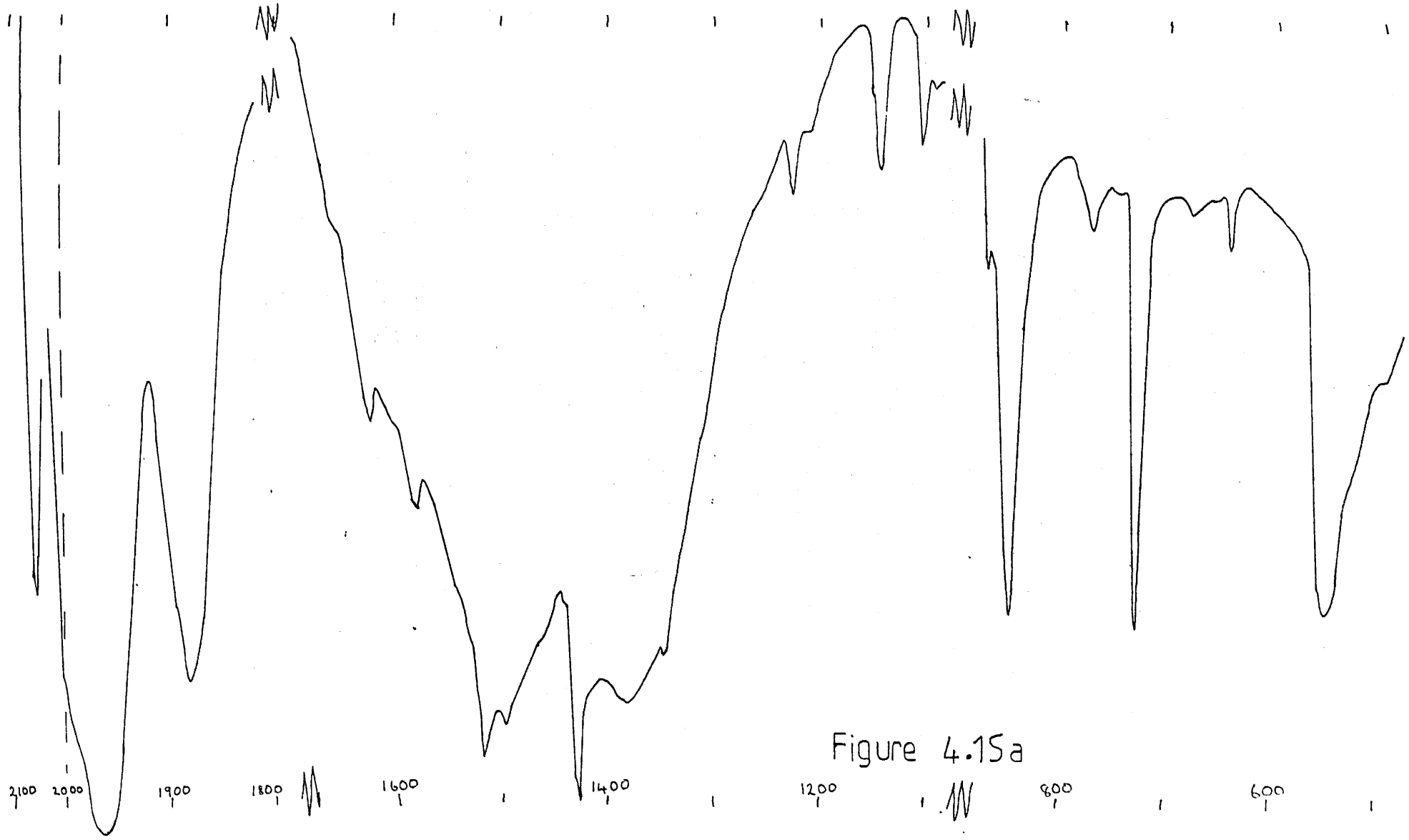


Figure 4.15a

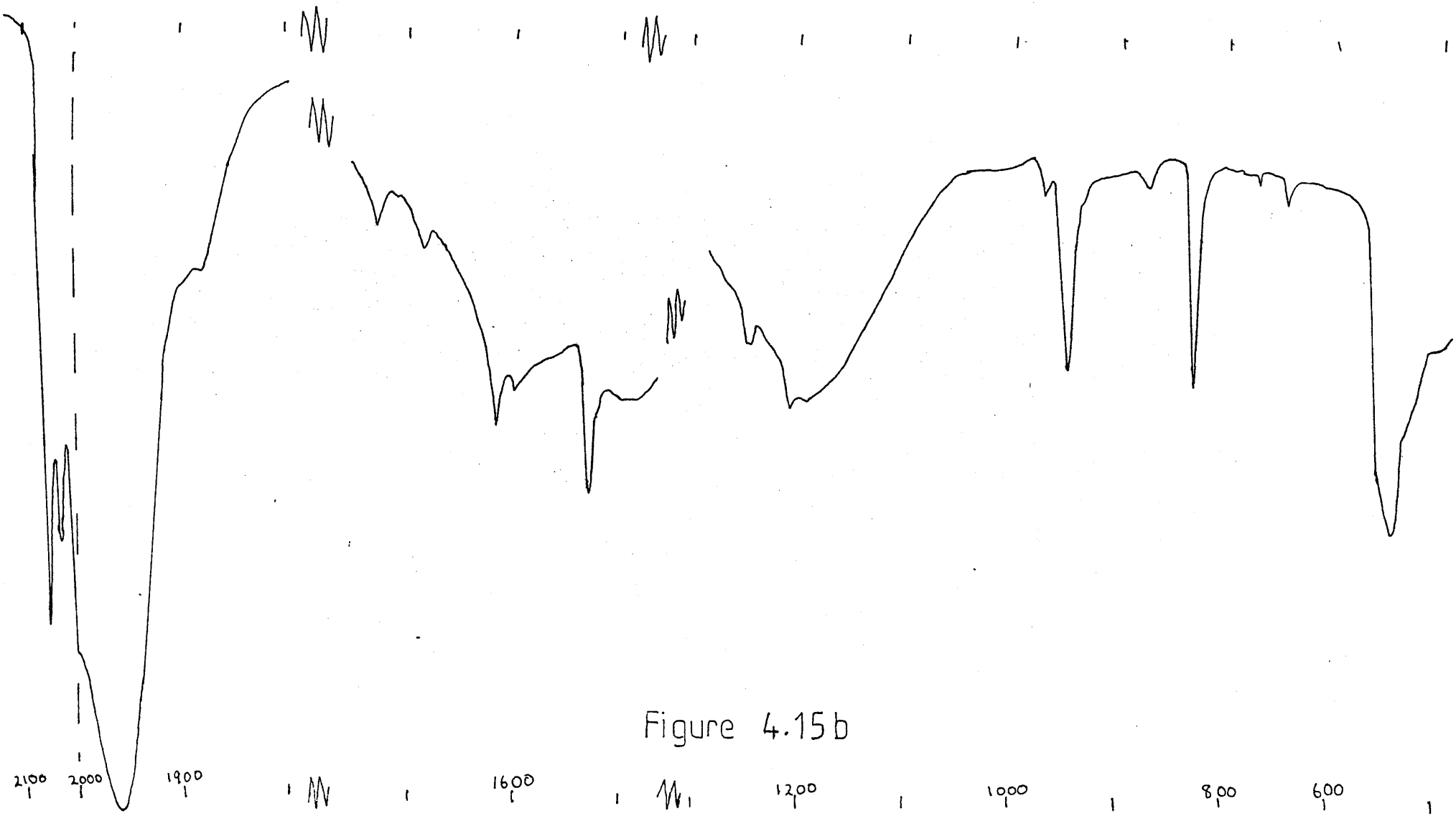


Figure 4.15 b

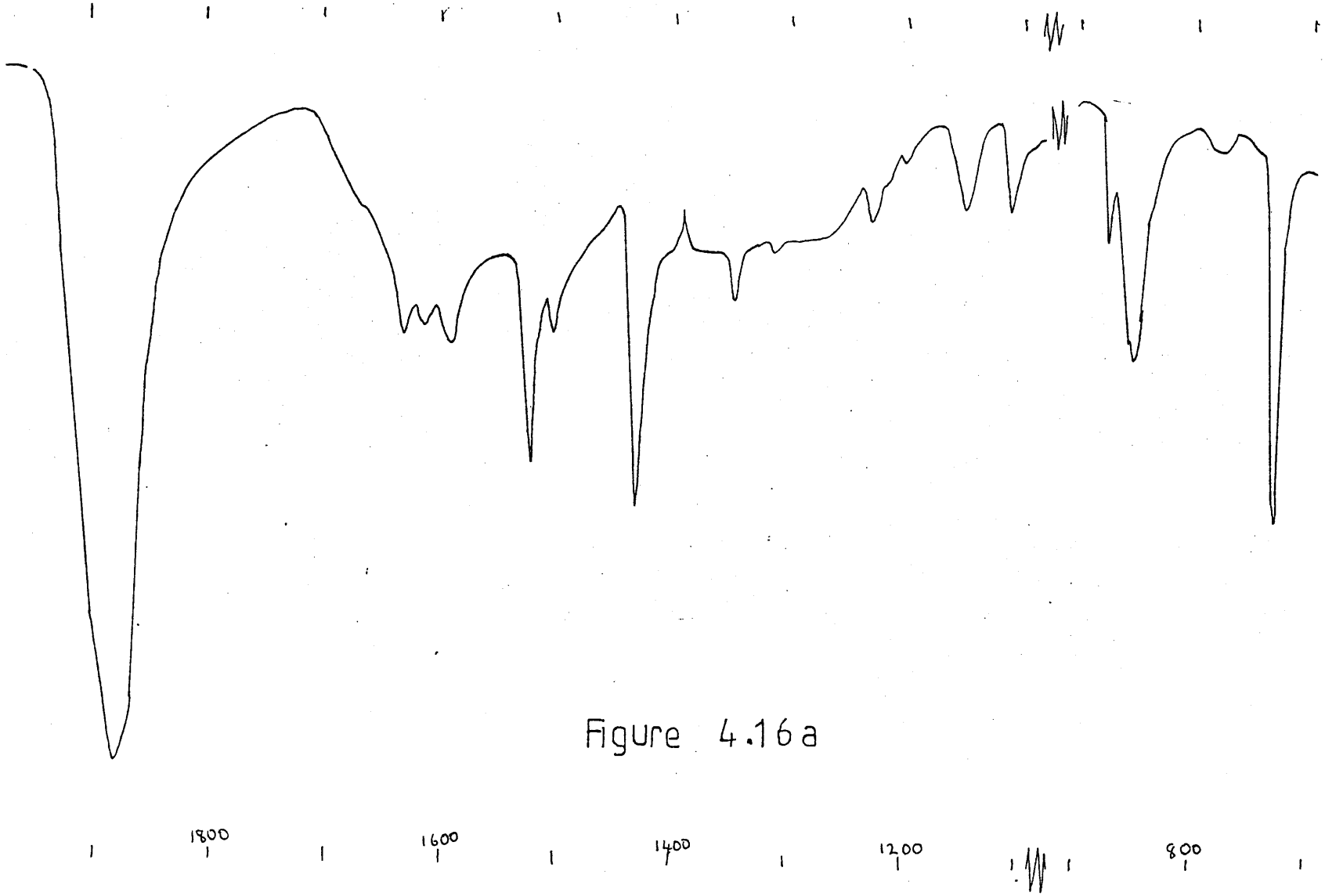


Figure 4.16a

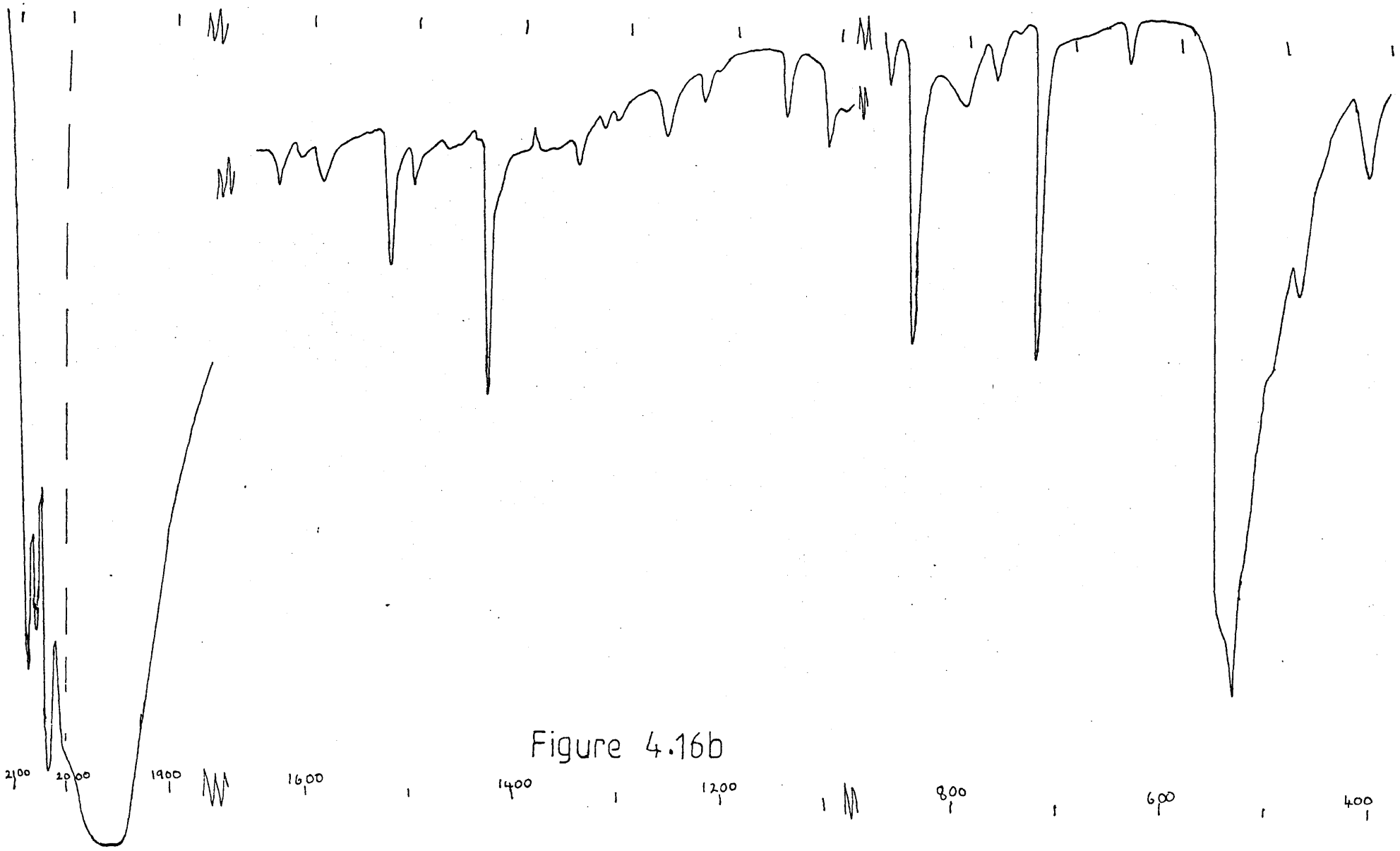


Figure 4.16b

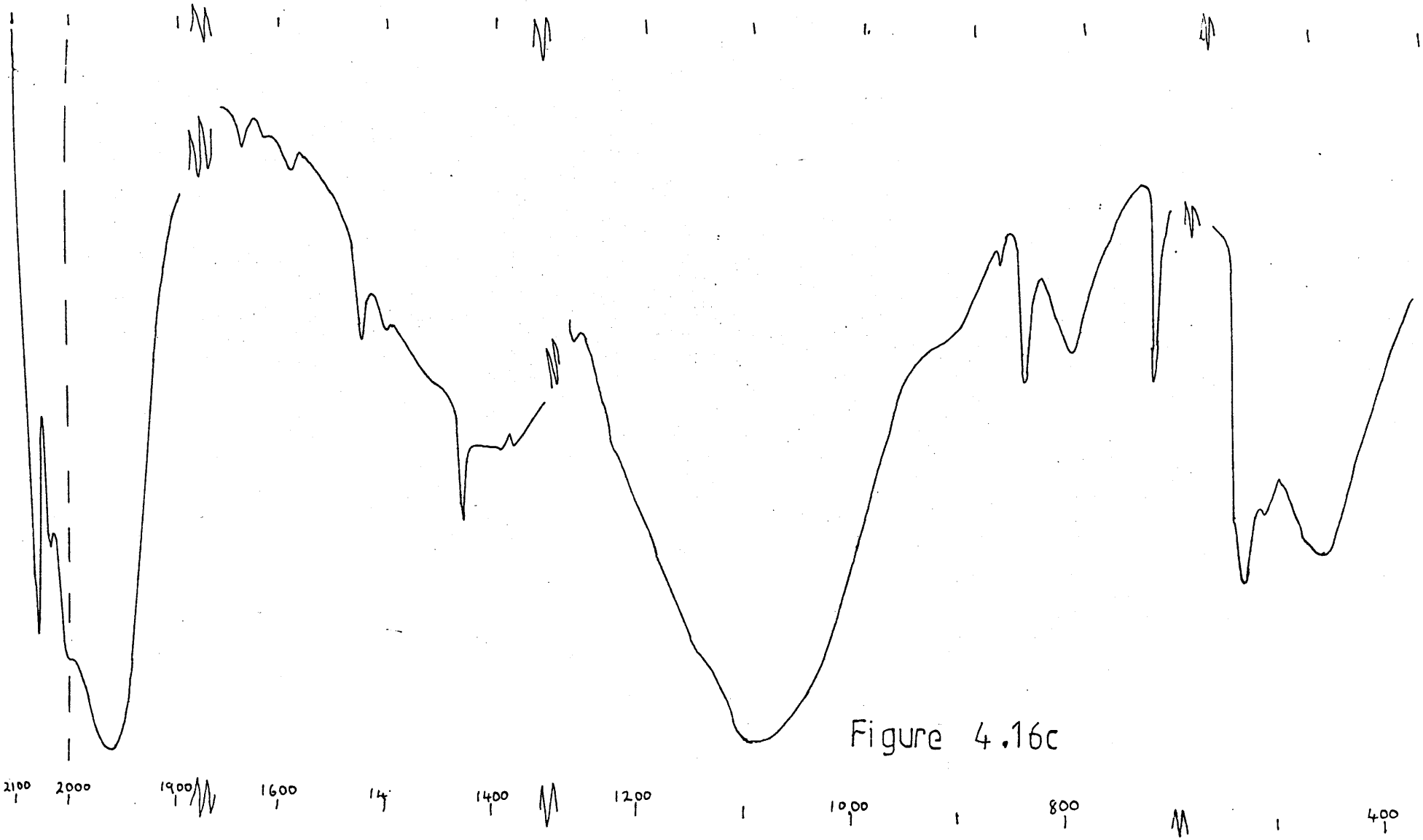


Figure 4.16c

On filtration, at the water pump, sandy coloured crystals and an orange filtrate were obtained. Further filtration gave sandy - yellow crystals and a pink filtrate, colour attributable to $[Co(H_2O)_6]^{2+}$. The solid was washed with a little water and dried before its i.r. spectrum was recorded.

2) Reaction of $Hg[Co(CO)_4]_2$ with Sodium Amalgam in Ethereal Solvents.

Since sodium amalgam was being used, the flask required for experimental work was the same as that described in Fig. 3.15, again fitted with a link stirrer and gas inlet and outlet. A typical experiment is outlined below, using T.H.F. as the solvent.

1.98g $Hg[Co(CO)_4]_2$ [3.65×10^{-3} moles] was added to 50 ml freshly distilled solvent, under nitrogen, to give an orange suspension. Roughly 6g fresh sodium amalgam was poured in [0.1g Na and 6g Hg give 1.5% Na in the amalgam] leading to a redder solution. After three hours stirring of the mercury layer the solution was filtered into a flask containing 70 ml aqueous $Fe(\underline{o}phen)_3Cl_2$ [0.025 M] and stirred for twenty minutes. (This is a deviation from Burlitch's work up; at this stage they exposed the solution to air for a short time to rid it of any $[Co(CO)_4]^-$). The mixture was decanted into a separating funnel, 80 ml deionised water added, then left to separate into a red oil and an aqueous phase. The oil was collected, dissolved in 20 ml ethanol and then 100 ml deionised water added to the red solution to precipitate the orange solid product. This could now be collected, by filtering at the water pump, washed with a little hexane, dried, and its i.r. spectrum recorded.

This method was used for the $[Ni(\underline{o}phen)_3]^{2+}$ derivatives, with of course $Ni(\underline{o}phen)_3Cl_2$ being substituted for the analogous iron compound.

When diethyl ether was the solvent, there was a further complication. After the filtration of the reaction mixture into $Fe(\underline{o}phen)_3Cl_2$, a red solid came out of solution which comprised $[Co(CO)_4]^-$ ions. This is

hardly surprising since it has already been demonstrated that large cations will precipitate $[Co(CO)_4]^-$ from diethyl ether solutions.

3) Reaction of $Hg[Co(CO)_4]_2$ with Allyl Bromide.

To 50 ml, carbon monoxide saturated, freshly distilled T.H.F., 0.814g $Hg[Co(CO)_4]_2$ [1.50×10^{-3} moles] was added while stirring, forming a green / yellow solution and solid. 170μl allyl bromide [1.96×10^{-3} moles] was syringed into the flask with a little gas evolution, and the solution became slightly greener. Overnight there was no evidence, by i.r., of reaction although the solution was now orange / yellow with the green / yellow solid (undissolved $Hg[Co(CO)_4]_2$). No further change was noted over the next five days.

4) Reactions of $Co_2(CO)_8$ and Sodium Amalgam in Diethyl Ether.

For the reaction of a large amount of $Co_2(CO)_8$ with sodium amalgam, originally planned to give reduction to $[Co(CO)_4]^-$ (!), typically 1.21g $Co_2(CO)_8$ [3.54×10^{-3} moles] was added to 100 ml sodium dried diethyl ether which already had 150 g sodium amalgam (1% Na) present. The reaction vessel used was that described in Fig. 3.15. Initially the solution was dark brown, with slight effervescence, becoming oranger in hue over the next five hours, along with some dark solid. Overnight a red yellow / brown colouration came into being (in an i.r. cell of 0.1 mm pathlength it appears mustard yellow) and more solid had been produced. The i.r. spectrum remained complicated. Addition of a few drops of deoxygenated, deionised water did not alter the colour of solution. These results can be compared with the weaker solutions used in chapter 3.

The work was repeated using a less concentrated solution of $Co_2(CO)_8$. Using the same experimental set-up, 0.512g $Co_2(CO)_8$ [1.50×10^{-3} moles] was added to 75 ml diethyl ether and sodium amalgam. After twenty hours a blood red solution resulted, showing mainly $[Co(CO)_4]^-$ and a little

$[Co_3(CO)_{10}]^-$. 0.167g LiBr [1.92×10^{-3} moles] was added to give an opaque red solution, but appeared not to have any other effect on the reaction.

5) Reaction of $Co_2(CO)_8$ with Mercury in Diethyl Ether.

Using the special reaction vessel, 0.514g $Co_2(CO)_8$ [1.50×10^{-3} moles] was placed, along with 30.27g mercury [0.15 moles], in 70 ml diethyl ether, under a carbon monoxide flow. The dark brown solution appeared unreactive after four hours and so a further 39.84g mercury [0.199 moles] was added, giving a total of 0.349 moles mercury in the reaction flask. This only led to a slight reddening of the solution with the i.r. spectrum showing evidence of $Hg[Co(CO)_4]_2$. Finally 0.168g LiBr [1.93×10^{-3} moles] was added, four hours after the reaction had started, giving a dark orangy / brown solution (bright green / yellow in the i.r. cell) and an i.r. indicative of $\{Hg[Co(CO)_4]_2X\}^-$ where X = $Co(CO)_4$, Br or Cl - more definite assignment is not possible - and a little $Hg[Co(CO)_4]_2$. At this point the elemental mercury left was run off and the only change over the next 24 hours was an increase in the concentration of $Hg[Co(CO)_4]_2$.

Adding LiBr later in the reaction gave $Li^+[Co(CO)_4]^-$ in solution in addition to the other species noted above.

6) Isolation of Products of $Co_2(CO)_8$ and Mercury in Ethereal Solvents.

The type of experiment outlined in part(5) above was repeated and some of the products isolated using $Fe(o\text{phen})_3Cl_2$.

2g $Co_2(CO)_8$ [5.85×10^{-3} moles] and 220g mercury [1.10 moles] were put into 120 ml dried diethyl ether with 0.671g LiBr [7.73×10^{-3} moles] added ten minutes later, giving a red / brown solution. Two hours later the mercury was run off and the solution filtered, under carbon monoxide, into 70 ml 0.025 M squeous $Fe(o\text{phen})_3Cl_2$. After stirring for fifteen minutes this was transferred to a separating funnel and allowed to stand.

The red oil which separated was dissolved in 20 ml ethanol and after five minutes had separated to give a red solid and red solution, WITHOUT THE ADDITION OF WATER. This was filtered and the solid proved to be the simple salt of $[Co(CO)_4]^-$ - (see Fig. 4.14c). 100 ml of water was added to the filtrate but failed to produce more solid. Meanwhile a solid had been formed in the separating funnel which, from its i.r. spectrum, proved to be a mixture of $[Co(CO)_4]^-$ and $\{Hg[Co(CO)_4]_3\}^-$ - (Fig. 4.17).

Repeating the experiment gave $[Co(CO)_4]^-$ as before but the oil this time yielded $Hg[Co(CO)_4]_2$, presumably from decay of $\{Hg[Co(CO)_4]_3\}^-$. The work was repeated in T.H.F. using 50 ml T.H.F., under carbon monoxide, with 2.09g $Co_2(CO)_8$ [6.12×10^{-3} moles] and 155.15g mercury (0.77 moles). After half an hour 0.699g LiBr [8.05×10^{-3} moles] was added to the dark green / brown solution, intensifying the green colour, and left for three hours. Filtration into 70 ml aqueous $Fe(\underline{o}phen)_3Cl_2$ followed to give a red solution and a dark solid. Working up the solution as described in part(2) gave brownish crystals while a brownish / red amorphous solid was isolated from the aqueous layer. The crystals proved to contain a mixture of $[Co(CO)_4]^-$, $\{Hg[Co(CO)_4]_2X\}^-$ and an unknown species, with the amorphous solid showing evidence of $[Co(CO)_4]^-$ and $\{Hg[Co(CO)_4]_2X\}^-$. In both cases, X was a mixture of Cl and Br, there being a slight difference in the i.r. spectra from previous examples.

Repeating this work with more mercury present and LiBr added at the same time as the other reagents, gave $\{Hg[Co(CO)_4]_3\}^-$ as the major product with some $\{Hg[Co(CO)_4]_2X\}^-$, X = Br or Cl, present. If $Ni(\underline{o}phen)_3Cl_2$ is used in the latter stages a mixture of $[Co(CO)_4]^-$, $\{Hg[Co(CO)_4]_3\}^-$, $\{Hg[Co(CO)_4]_2X\}^-$ and $Hg[Co(CO)_4]_2$ is found.

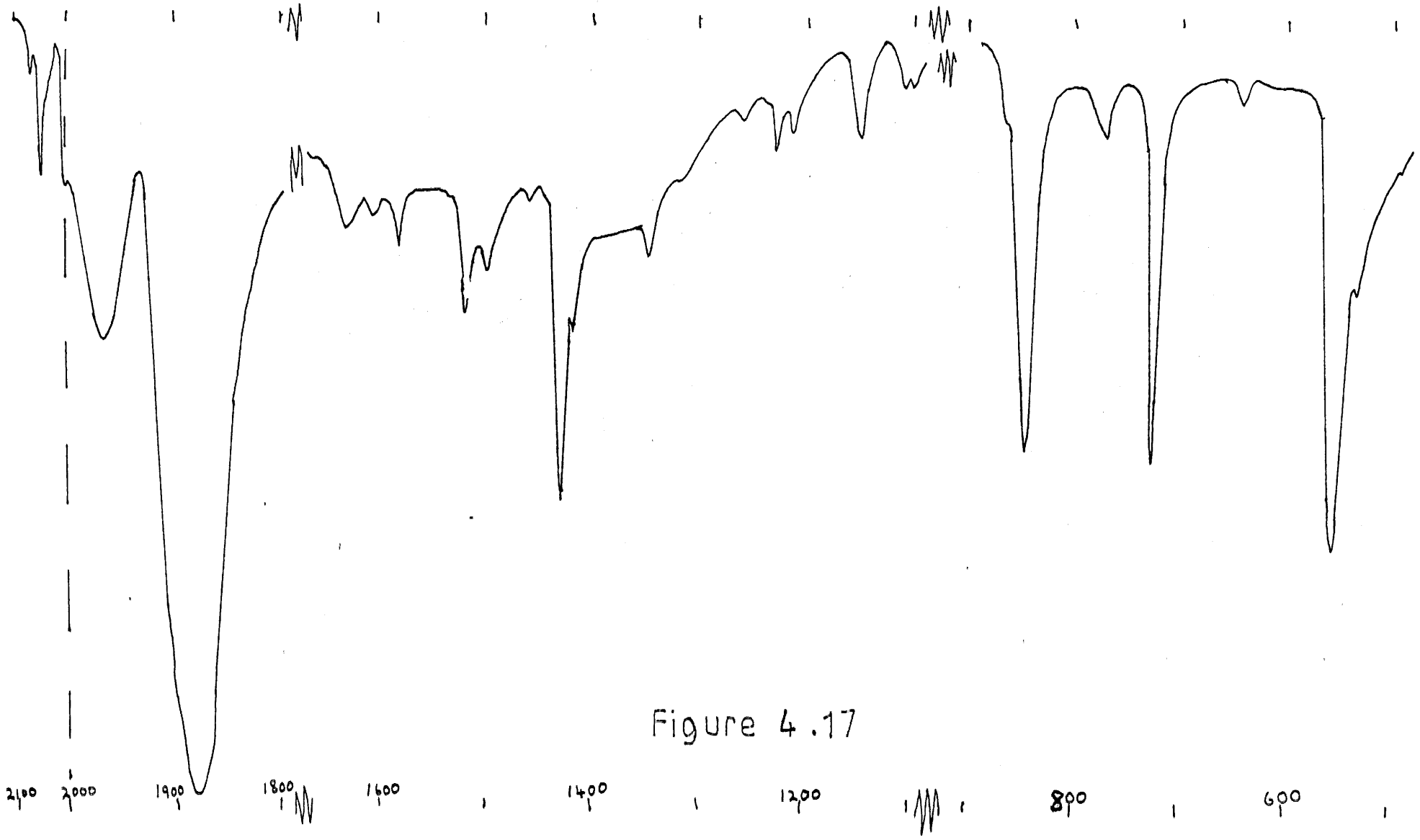


Figure 4.17

5. DISCUSSION.

The main point to arise from the work of this chapter is that $Co_2(CO)_8$ and mercury containing compounds do not react to give one or two simple products. When taken in conjunction with chapter 3 these results have shown that direct reduction of $Co_2(CO)_8$ by amalgam, to some extent in T.H.F. and to a very large extent in diethyl ether, is not the only reaction pathway, if in fact it is a pathway at all. We believe that reaction of $Co_2(CO)_8$ under these condition is due to disproportionation not reduction. As early as 1970, Edgell et al. showed that under rigorously anhydrous conditions $Co_2(CO)_8$ and sodium amalgam in T.H.F. only gave $NaCo(CO)_4$ after several weeks, which was identical to the time required for solvent induced reaction[254]. Yet very recently it was reported that

'A $NaCo(CO)_4$ solution in 40 ml diethyl ether was prepared from 0.341g $Co_2(CO)_8$ [1 m mol] and 40g 1.5% sodium amalgam' [281]

The only conclusion that can be drawn from that statement is that the authors did not require very anhydrous conditions and so water present led to disproportionation.

The results presented in this chapter have shown that a mixture of products is obtained dependent upon the exact point at which the reaction was halted. In diethyl ether solutions, on addition of $M(\underline{o}phen)_3Cl_2$, M = Fe or Ni, there was precipitation of the red salt of $[Co(CO)_4]^-$. With reference to chapter 2, this is rationalised in terms of the large cation making the anion insoluble in solution. Elsewhere a mixture of $Hg[Co(CO)_4]_2$, $\{Hg[Co(CO)_4]_3\}^-$ and the species assigned to $\{Hg[Co(CO)_4]_2X\}^-$ (X = Cl, or Cl and Br) was found, with the latter two being isolated on separate occasions as the only complex present (from T.H.F. solutions). $\{Hg[Co(CO)_4]_2X\}^-$ was only found in reactions with T.H.F. as the solvent. Diethyl ether again proved to give a more

complicated system; apart from $[Co(CO)_4]^-$ coming out of solution, there was never one species only in any product isolated. Because these species are closely related, no attempt was made to separate them. The other interesting solid isolated was $[Fe(\underline{o}phen)_3][Co_3(CO)_{10}]_2$, obtained from the aqueous layer of the work up. Since it was not in evidence at earlier stages of the reaction it is presumed that air oxidation of $[Co(CO)_4]^-$, which is soluble in water, has occurred and the large cation present has stablilised $[Co_3(CO)_{10}]^-$ by precipitation. In diethyl ether itself any $[Co(CO)_4]^-$ present crashes out of solution upon addition of $Fe(\underline{o}phen)_3Cl_2$ but in T.H.F. it is dispersed between both phases and so salts of the anion or its derivatives are obtained from the aqueous phase. Using $Ni(\underline{o}phen)_3Cl_2$ instead of the iron compound appears to be more favourable towards $[Co(CO)_4]^-$ being present in the aqueous phase.

For the reaction of $Co_2(CO)_8$ and mercury in diethyl ether, a simple reaction sequence has been constructed and is shown in Fig. 4.18.

$$Hg + Co_2(CO)_8 \xrightarrow{Et_2O} Hg[Co(CO)_4]_2 + Co_2(CO)_8 \xrightarrow{LiBr} Li^+ + \{Hg[Co(CO)_4]_3\}^-$$

$$\{Hg[Co(CO)_4]_3\}^- \xleftarrow[\text{oxidation}]{\text{few days}} Hg[Co(CO)_4]_2 + Li^+$$

Figure 4.18

The new species which has been assigned the formula $\{Hg[Co(CO)_4]_2X\}^-$ was first observed when it was realised that the i.r. signal at 2060 cm^{-1} was not due to unreacted $Hg[Co(CO)_4]_2$. On closer inspection the presence of this band coincided with a shoulder, around 2005 cm^{-1}, on the very intense broad signal of $\{Hg[Co(CO)_4]_3\}^-$, at 1950 - 1970 cm^{-1}. Although the literature values are not in perfect agreement[274], it would seem reasonable that a species intermediate between $Hg[Co(CO)_4]_2$

and $\{Hg[Co(CO)_4]_3\}^-$ is the cause of this extra signal at 2060 cm^{-1} which happens to be intermediate between the 2070 cm^{-1} and 2040 cm^{-1} signals of these two respective species e.g. $\{Hg[Co(CO)_4]_2X\}^-$ (lit. value $\{Hg[Co(CO)_4]_2Cl\}^-$ in T.H.F. : 2071w, 2048s, 1979vs, 1896vw - due to $[Co(CO)_4]^-$). Here a $[Co(CO)_4]^-$ group of $\{Hg[Co(CO)_4]_3\}^-$ has been replaced by a halide, either Cl^- from $Fe(\underline{o}phen)_3Cl_2$ or Br^- from LiBr where this is present. The halogen is more electron withdrawing than the $Co(CO)_4$ group and so will perpetrate a shift to higher wavenumber w.r.t. $\{Hg[Co(CO)_4]_3\}^-$.

For the simple reaction of sodium amalgam with $Co_2(CO)_8$ in diethyl ether the i.r. spectra were not very conclusive, because of the initial high concentration of $Co_2(CO)_8$ giving rise to two intense absorptions. By comparing the spectra with similar experiments discussed in chapter 3, it was obvious that the same type of species in solution were being observed viz. when $[Co(CO)_4]^-$ is dominating the spectrum in a very dry solution it is strongly perturbed as shown by the pronounced shoulder (virtually a separate signal in its own right) of the main signal.

For ease of reference, the results of the foregoing reactions have been collected together in Table 4.2.

Mercury - cobalt compounds are well documented. Apart from those already mentioned in the introduction $[Co(CO)_4(HgCH_2SiMe_3)]$ is known and its i.r. spectrum closely resembles that of $[Co(CO)_4(HgMe)]$, showing the lack of influence of the CH_2SiMe_3 group on the molecular geometry[282]. This will slowly react in $CDCl_3$ solutions (50% over one month at 20°C, 100% over two hours at 80°C) to give:

$$2[Co(CO)_4(HgCH_2SiMe_3)] \longrightarrow Hg(CH_2SiMe_3)_2 + Hg[Co(CO)_4]_2 \qquad (4.11)$$

Finally, it is not recommended to attempt formation of $[Co(CO)_4]^-$ by sodium amalgam reduction of $Co_2(CO)_8$ in anhydrous conditions, especially when using diethyl ether. Rather it has been shown that alkali metal

Reactants	Solvent	Metal Cation[a]	Products[b]
$Co_2(CO)_8$, Hg, LiBr	T.H.F.	Fe	$\{Hg[Co(CO)_4]_2X\}^-$ (X=$Co(CO)_4$, Cl, Br); $[Co(CO)_4]^-$; unknown species
$Co_2(CO)_8$, Hg, LiBr	T.H.F.	Ni	$\{Hg[Co(CO)_4]_2X\}^-$ (X=$Co(CO)_4$, Cl, Br); $[Co(CO)_4]^-$; $Hg[Co(CO)_4]_2$;
$Co_2(CO)_8$, Hg, LiBr	Et_2O	- [c]	$\{Hg[Co(CO)_4]_2X\}^-$ (X=$Co(CO)_4$ or Cl and Br);
$Co_2(CO)_8$, Hg, LiBr	Et_2O	Fe	$Hg[Co(CO)_4]_2$; traces of $\{Hg[Co(CO)_4]_3\}^-$? ; $[Co(CO)_4]^-$;
$Co_2(CO)_8$, Na/Hg	Et_2O	- [c]	$\{Hg[Co(CO)_4]_3\}^-$; $[Co(CO)_4]^-$; $[Co_3(CO)_{10}]^-$; unidentified species;
$Co_2(CO)_8$, Na/Hg, LiBr	Et_2O	- [c]	$[Co(CO)_4]^-$; $[Co_3(CO)_{10}]^-$;
$Hg[Co(CO)_4]_2$, Na/Hg	T.H.F.	Fe	$\{Hg[Co(CO)_4]_2X\}^-$ (X=$Co(CO)_4$ and Cl); $[Co_3(CO)_{10}]^-$;
$Hg[Co(CO)_4]_2$, Na/Hg	T.H.F.	Ni	$\{Hg[Co(CO)_4]_2X\}^-$ (X=$Co(CO)_4$ and Cl); $[Co(CO)_4]^-$;
$Hg[Co(CO)_4]_2$, Na/Hg	Et_2O	Ni	$\{Hg[Co(CO)_4]_3\}^-$;

a Metal cation in $[M(\underline{o}phen)_3]^{2+}$; b Solid products unless stated otherwise; c Solution mixture, no solid products.

i.r. of species (in the solid form) encountered in these experiments

$[Co(CO)_4]^-$ - 2005w, 1880vs ; $Co_3(CO)_{10}^-$ - 2015vs, 1960m ;

$Hg[Co(CO)_4]_2$ - 2075s, 2040m, 2010 (shoulder), 1970vs ; $\{Hg[Co(CO)_4]_3\}^-$ - 2035s, 1970 - 1950vs, broad.

$\{Hg[Co(CO)_4]_2X\}^-$ - 2060s, 2010 (shoulder), 1970vs. (X = Cl, Br).

a Cation of the anionic compounds is $[Fe(\underline{o}phen)_3]^{2+}$; b in the carbonyl region 2200 - 1800 cm^{-1}

Table 4.2

reduction is more feasible. As early as 1952 it had been demonstrated that a liquid ammonia solution of sodium will reduce $Co_2(CO)_8$ to anion[261] and lithium wire plus $Co_2(CO)_8$ gives $LiCo(CO)_4$ [160]. In diethyl ether formation of $[Co_3(CO)_{10}]^-$ instead of $[Co(CO)_4]^-$ is highly likely (see preceeding chapter). An alternative reduction route, given by Cleland et al., requires $Hg[Co(CO)_4]_2$ and sodium metal in excess, giving both $[Co(CO)_4]^-$ and a deposit of elemental mercury[277], according to Fig.4.19.

$$Hg[Co(CO)_4]_2 + 2Na \longrightarrow 2NaCo(CO)_4 + Hg$$

$$NaCo(CO)_4 + Hg[Co(CO)_4]_2 \longrightarrow Na\{Hg[Co(CO)_4]_3\} \xrightarrow{2Na} 3NaCo(CO)_4 + Hg$$

Figure 4.19

The same group also showed that $[(PBu_3)_2Co(CO)_3][Co(CO)_4]$ can react with $Hg[Co(CO)_4]_2$ in diethyl ether to give a solid whose i.r. spectrum is identical to that of $\{Hg[Co(CO)_4]_3\}^-$ thus proving that this anion can be prepared by more than one process. This solid could in turn react with Ph_3P in T.H.F. to give the substituted derivative $Hg[Co(CO)_3PPh_3]_2$:

$$\{Hg[Co(CO)_4]_3\}^- \rightleftharpoons Hg[Co(CO)_4]_2 + [Co(CO)_4]^- \xrightarrow{2Ph_3P} Hg[Co(CO)_3PPh_3]_2 \qquad (4.12)$$

During the course of experiments in this laboratory, reduction of $Co_2(CO)_8$ in diethyl ether and under carbon monoxide, using a sodium / copper couple failed to give any conclusive results and because of a shortage of time, could not be repeated.

The only other reasonable alternative to reduction for generation of $[Co(CO)_4]^-$ in the absence of nucleophiles such as halides is to use NaOH. Edgell et al. have done this but, of course, due to the nature of NaOH it is impossible to have very anhydrous conditions[254]. The only way round this problem is to form $NaCo(CO)_4$, remove all traces of solvent, then redissolve the white solid in dry solvent. As yet there is no quicker or simpler route to guarantee pure, anhydrous $NaCo(CO)_4$ in solution.

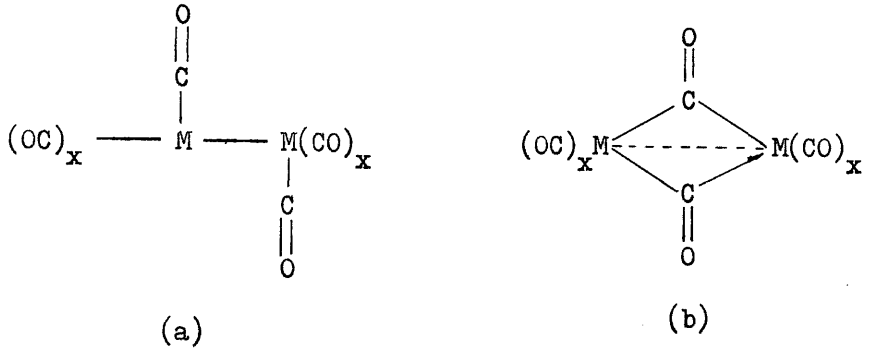
CHAPTER 5

TETRACOBALT DODECACARBONYL AND ITS REACTIONS

CHAPTER 5 - TETRACOBALT DODECACARBONYL AND ITS REACTIONS

1. INTRODUCTION

In polynuclear metal complexes containing more than two metals, there are two extreme ways of linking the metal atoms, as shown in Fig.5.1[235].



(a) (b)

Figure 5.1

In (a) the carbonyl formally donates two electrons to one metal only and an unsupported M - M bond pairs the odd electron of each metal. In (b) each bridging carbonyl donates a single electron to each metal, with spin pairing then assumed to occur via a M - M bond (originally to explain the diamagnetism of such compounds), although coupling through the bridging carbonyls is possible. Generally first row transition metals favour (b) while the second and third row elements prefer (a), although there are exceptions e.g. $Mn_2(CO)_{10}$. When bridging carbonyl structures do occur the type of metal atoms involved are short of the required number of electrons for the E.A.N. rule, usually by one, and so the M - M bond is postulated.

$Co_4(CO)_{12}$, a polynuclear carbonyl, has been known since the days of $Co_2(CO)_8$ although its molecular structure was in doubt. Mond et al. referred to the $Co(CO)_3$ compound in 1910[23] and Hieber also referred to the polymer of $Co(CO)_3$[60].

The simplest way to obtain $Co_4(CO)_{12}$ is to decarbonylate $Co_2(CO)_8$ by stewing it up for some hours in an inert atmosphere (a carbon monoxide

atmosphere will, of course, suppress carbon monoxide loss from the starting material). In the more sterically crowded alcohols isopropanol and tert-butanol, Chini and Albano found that $Co_4(CO)_{12}$ is formed preferentially to $[Co(B)_6][Co(CO)_4]_2$ where B = methanol or ethanol[136]. The same authors also prepared $Co_4(CO)_{12}$ using dioxane and T.H.F. In each case the solvent and $Co_2(CO)_8$ were boiled, under solvent vapour pressure, around 40 - 60°C for up to twenty four hours, the carbon monoxide being pumped off periodically. An even more exotic route involved irradiation of solutions of $HCCo_3(CO)_9$, under a hydrogen atmosphere, with U.V. or visible light, to surrender $Co_4(CO)_{12}$ and methane[283]. A more simple method, and the technique used in this laboratory, was to reflux $Co_2(CO)_8$ at 55 - 60°C overnight in hexane, under nitrogen. At high temperatures (above 100°C) decomposition of $Co_4(CO)_{12}$ to cobalt metal and carbon monoxide occurs.

As outlined in chapter 1, the structure of $Co_4(CO)_{12}$ has aroused some controversy with the C_{3v} crystalline structure not apparently carrying over to its solution structure. Further work, including high temperature ^{13}C studies, later indicated a C_{3v} structure persisted in solution[101]. Cotton et al. confirmed the disorder in the crystal structure, with the apparent molecular unit consisting of two superposed half molecules, leading to problems of refinement of the structure[284].

A host of spectroscopic techniques have been applied to the $Co_4(CO)_{12}$ molecule. The negative - ion mass spectra of tetranuclear carbonyl clusters have been recorded[285]. At 70eV, $Co_4(CO)_{12}$ displays the behaviour usually shown by the metal carbonyls with the rare gas configuration. The molecular negative - ion is absent and a low number of ions formed upon loss of carbonyl groups, and containing the four metal atoms, is present. The ^{59}Co n.m.r. spectrum of $Co_4(CO)_{12}$ in solution was determined in 1967, in a bid to solve its structure, and

favoured C_{3v} symmetry[267,286]. More recently the ^{17}O n.m.r. spectrum has been obtained[287]. This technique compares favourably with ^{13}C n.m.r. studies with similar ranges and ordering of chemical shift, and having the advantage of more favourable line widths for cobalt derivatives, allowing an extension of the range of temperatures in which fluxional dynamics information can be derived.

The i.r. spectrum of $Co_4(CO)_{12}$ in heptane was reported in 1955 and this was used to deduce that the compound contained two types of carbonyl in a 2:1 ratio of terminal : bridged[85]. One of the earliest in depth i.r. investigations of $Co_4(CO)_{12}$ was by Bor[89]. Using a very concentrated solution of $Co_4(CO)_{12}$ in hexane, to increase the low intensity absorptions in the 2100 - 2120 cm^{-1} region, Bor tabulated the i.r. signals as shown in Table 5.1

Frequency and Relative Intensity Values of the C - O Stretching Bands of $Co_4(CO)_{12}$ in n-Hexane:

$\bar{\nu}$ (CO)cm^{-1}	Relative Intensity
2104.4	~ 0.05
2063.2	9
2054.5	10
~2048	-
2037.9	0.6
2027.5	0.8
1997.2	^{13}CO, ~ 0.05
1898.4	0.04
1867.0	3.3
~ 1832	^{13}CO, ~ 0.05

TABLE 5.1

This meant that five of the possible terminal and the two bridging carbonyl stretching bands, for C_{3v} symmetry, had been observed.

Using matrix isolation techniques the i.r. spectrum of $Co_4(CO)_{12}$ also indicated a structure consistent with C_{3v} symmetry.

With so many ligands around the central metal core there is plenty of scope for fluxional type behaviour. It has been proposed that the variety of carbonyl scrambling observed in $M_4(CO)_{12}$ compounds can be attributed to a single type of process involving a cubo-octahedron intermediate; this has been comprehensively discussed[101].

$Co_4(CO)_{12}$ will react with EtOH giving $[Co(CO)_4]^-$ (in a pink solution, colour courtesy of Co^{2+})[136]. It can also be reduced by alkali metals (Li, Na or K) in T.H.F. to give the anion $[Co_6(CO)_{14}]^{4-}$ via the intermediate $[Co_6(CO)_{15}]^{2-}$. In this reaction an alternative reducing agent is cobaltocene[134]. These reactions are represented by equations 5.1 and 5.2.

$$5Co_4(CO)_{12} + 16M \longrightarrow 2\{M_4^+[Co_6(CO)_{14}]^{4-}\} + 8\{M^+[Co(CO)_4]^-\}$$

M = alkali metal (5.1)

$$9Co_4(CO)_{12} + 20cp_2Co \longrightarrow 4[cp_2Co]_2[Co_6(CO)_{15}] + 12[cp_2Co][Co(CO)_4]$$

using cobaltocene (5.2)

Earlier it had been reported that alkali metals and $Co_4(CO)_{12}$ gave $[Co(CO)_4]^-$ salts[85]. With $LiCo(CO)_4$ itself, $Co_4(CO)_{12}$ will form $2Li[Co_3(CO)_{10}]$ in diethyl ether under argon[237], while decomposition of $Co_3(CO)_9C$-OH in diethyl ether by heat will give $Co_4(CO)_{12}$[238].

The newest reaction to involve $Co_4(CO)_{12}$ is its reduction by a four-fold excess of sodium carbide, Na_2C_2, to give $[Co_6(CO)_{14}]^{4-}$ with $[Co(CO)_4]^-$ the only other carbonyl containing compound[288]. This reaction in T.H.F., under nitrogen, took four days to reach completion at room temperature.

A series of $[Co_4(CO)_{11}X]^-$ compounds, X = Br, I or SCN, were synthesised with a view to investigating if such compounds were intermediates in the halide catalysed degradation of $Co_4(CO)_{12}$ to $Co_2(CO)_8$[289]. Using dichloromethane, CH_2Cl_2, as the solvent and at 0^oC, the equilibrium

according to equation 5.3 was established:

$$Co_4(CO)_{12} + I^- \rightleftharpoons [Co_4(CO)_{11}I]^- + CO \qquad (5.3)$$

If carbon monoxide is the atmosphere, the percentage of each compound remains unchanged but using nitrogen completely shifts the equilibrium to the right.

To precipitate the anion as the $[NEt_4]^+$ salt, only some n-heptane need be added, while stirring. Although the salt itself is stable in CH_2Cl_2 at -70°C, at room temperature, complete decomposition occurs within a couple of days, probably due to the following equation (where B = Lewis base):

$$3[Co_4(CO)_{11}I]^- + 4nB \longrightarrow 4[CoB_n][Co(CO)_4]_2 + 3I^- + CO \qquad (5.4)$$

To obtain the Br^- anion requires use of NEt_4Br or $PMePh_3PB$; the SCN^- salt is obtained by addition of $[N(PPh_3)_2][SCN]$. These anions have also been isolated by addition of heptane at -70°C but being more labile, they only require a few hours at room temperature to decompose. In all cases disproportionation is accelerated by using Lewis base solvents such as T.H.F.

From the i.r. of those compounds, the X group appears to replace a terminal carbonyl group of the apical cobalt atom of $Co_4(CO)_{12}$.

Na $[Co_4(CO)_{11}(COOR)]$ was also prepared using $Co_4(CO)_{12}$ and NaOR in alcohol at -70°C. Any water present immediately hydrolysed this species, i.e.

$$[Co_4(CO)_{11}COOR]^- + H_2O \longrightarrow Co_4(CO)_{12} + ROH + OH^-, \; R = Me, Pr^i \qquad (5.5)$$

Further reaction between $Co_4(CO)_{12}$ and OH^- will then take place.

A similar method was used to prepare $[NH_3Pr^n][Co_4(CO)_{11}(CONHPr^n)]$ from $Co_4(CO)_{12}$ and n-propylamine. The latter species, involving organic ligand substitution, are all purple - red whereas the earlier compounds were green - brown, suggesting a difference in structure with the purple - red compounds perhaps basal substituted derivatives (for steric reasons).

The X Ray determined structure of the I^- compound (as the $[NEt_4]^+$ salt) has been determined[290]. It has three edge bridging carbonyls, defining a basal triangle, and eight terminal carbonyls, two per metal atom. The iodine atom is terminally bonded to the apical cobalt atom and overall the structure is derived from the C_{3v} structure of $Co_4(CO)_{12}$. There are actually two isomers of this compound in the crystal studied, present in a 98:2 ratio. The minor constituent has the iodine in a basal position, causing a slight disorder in the structure of the compound. It is thought that I^- prefers the apical location to the basal position (as found in $[M_4(CO)_{11}I]^-$, M = Rh,Ir) because of electronic and steric effects. Cobalt has a lower electronegativity than the other metals so the two terminal ligands in the apical site can manage as well as the one terminal and two bridging ligands in the basal site. Thus steric effects become determining in this extreme case, unlike the other two derivatives. The energy difference between the two isomers is probably very small since both are present in the crystal. The mole ratio 49:1 of the two isomers is only thought to be a reflection of the solubility of the latter in the crystal lattice of the former, not an indication of the equilibrium between the isomers.

Phosphorus ligand substitution in $Co_4(CO)_{12}$ is almost as popular as in $Co_2(CO)_8$. The preparation and characterisation of $Co_4(CO)_{8-x}(PPh_3)_x(\mu_2\ CO)_2(\mu_4 PPh)_2$ has shown this compound to consist of four $Co(CO)_2$ groups in a cobalt - cobalt bonded rectangle with the shorter sides spanned by a symmetrical bridging carbonyl ligand[291], This tetramer is then capped above and below by quadruply bridging PPh ligands to give an octahedral like Co_4P_2 core. The $Co_4(CO)_{10}(PPh)_2$ compound, ignoring the phenyl rings, approximates to D_{2h} symmetry. If two Ph_3P ligands replace two carbonyl ligands, a cis configuration, w.r.t. the tetracobalt plane, ideally possessing C_2 symmetry, occurs with

a little distortion of the central core, ascribed to an electronic effect.

The kinetics of interconversion of $Co_2(CO)_8$ and and $Co_4(CO)_{12}$ has received a lot of attention. Since the co-existance of these two compounds in solution will be examined, it would be fruitful to spend a little time on this topic before passing on.

Sternberg et al. noted that the action of t-butyl alcohol on $Co_2(CO)_8$ evolved fewer moles of carbon monoxide than in MeOH or EtOH solutions, and some brownish / black crystals appeared[151]. The solution also contained no $[Co(CO)_4]^-$. The crystals proved to be $Co_4(CO)_{12}$, i.e.

$$2Co_2(CO)_8 \longrightarrow Co_4(CO)_{12} + 4CO \qquad (5.6)$$

The difference in reaction was attributed to steric effects.

Later Chini et al. proposed that $[Co(CO)_4]^-$ and $Co_2(CO)_8$ could be transformed into $Co_4(CO)_{12}$, explaining observations they had made[136] i.e.

$$2[CoB_6][Co(CO)_4]_2 + Co_2(CO)_8 \longrightarrow 2Co_4(CO)_{12} + 12B \qquad (5.7)$$

This would explain why in MeOH and EtOH, $[Co(CO)_4]^-$ derivatives were found but in the bulkier solvents ^{i}PrOH and ^{t}BuOH the Co(II) cation would be unfavourable and so formation of $Co_4(CO)_{12}$ occurred.

Ungváry and Markó then studied the interconversion in toluene[132b]. Based on their results they suggested the mechanism depicted in Fig.5.2.

$$Co_2(CO)_8 \underset{}{\overset{k_1}{\rightleftharpoons}} Co_2(CO)_7 + CO$$

$$Co_2(CO)_7 \overset{k_2}{\rightleftharpoons} Co_2(CO)_6 + CO$$

$$2Co_2(CO)_6 \xrightarrow[\text{slow}]{k_2} Co_4(CO)_{12}$$

Figure 5.2

Coordinatively unsaturated species were needed to form new Co - Co bonds, as had previously been shown in the reaction:

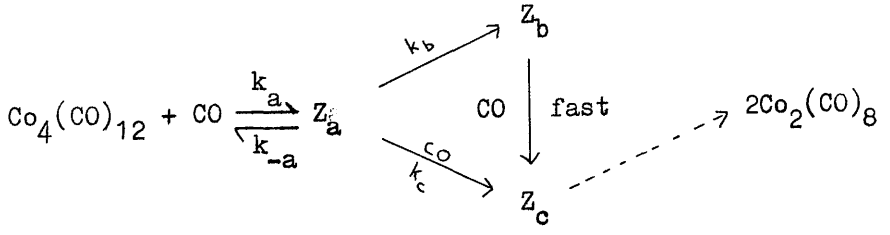
$$2HCo(CO)_4 \longrightarrow Co_2(CO)_8 + H_2 \qquad (5.8)$$

In this reaction $HCo(CO)_3$ was formed as the first step. The valid point was made that in nitrogen and at room temperature the formation of $Co_4(CO)_{12}$ from $Co_2(CO)_8$ containing solutions was significant and that use of carbon monoxide would minimise this. Chapter 2 of this thesis bears out this point of information.

The same authors next turned their attention to this reaction in heptane[132c]. Again $Co_2(CO)_7$ is formed in the first, pre-equilibrium, stage. They found that the kinetics of this transformation of $Co_2(CO)_8$ to $Co_4(CO)_{12}$ are strongly dependent on the solvent used; the order of concentration of carbon monoxide changes from -4 in toluene to -3 in heptene and to -2 in heptane with the reaction being second order w.r.t. $Co_2(CO)_8$ concentration.

Next to appear was a kinetic study of $Co_4(CO)_{12}$ with carbon monoxide to give $Co_2(CO)_8$ in n-hexane over a range of temperature and carbon monoxide pressure[292]. The reaction was found to be first order in $Co_4(CO)_{12}$ with the order in carbon monoxide concentration varying between one, at low pressure and high temperature, and two, at high pressure and low temperature. The reaction scheme of Fig. 5.3 was put forward, this being the simplest one which was consistent with experimental data.

"Path 1"



"Path 2"

Figure 5.3

Z_a would have molecular formula $Co_4(CO)_{13}$ and was visualised as occurring

by breaking one Co - Co bond and replacing it by a Co - CO bond while repositioning one bridging carbonyl group. Each cobalt would still conform to the E.A.N. rule.

Z_c would have molecular formula $Co_4(CO)_{14}$ which would involve breaking another M - M bond and the species would correspond to the dimer of $Co_2(CO)_7$. With regard to the hydroformylation reaction (equation 5.9), using lower temperature and carbon monoxide pressure will reduce the catalytic activity of $Co_2(CO)_8$ because of the difficult regeneration of $Co_2(CO)_8$ from $Co_4(CO)_{12}$. Even at high carbon monoxide pressures this conversion is unfavourable.

$$CH_2 = CH_2 + \tfrac{1}{2}Co_2(CO)_8 + H_2 \longrightarrow MeCH_2CHO + \tfrac{1}{4}Co_4(CO)_{12} \qquad (5.9)$$

Bor and Dietler then went on with the investigation using hexane as the solvent and a temperature range of 105 - 145°C, under carbon monoxide[293]. They established that $Co_2(CO)_8$ without the presence of carbon monoxide is thermally unstable, even at sub zero temperatures, although its conversion to $Co_4(CO)_{12}$ at this stage is kinetically very slow, as shown previously[132c]. At room temperature, even under a vacuum, this conversion is fast with a half life of around nine hours at 20°C and of one and a quarter hours at 28°C, in hydrocarbon solvents. At low carbon monoxide pressures $Co_4(CO)_{12}$ is the thermodynamically favoured compound. Recently, the thermal, photochemical and alcohol catalysed formation of $Co_4(CO)_{12}$ from $Co_2(CO)_8$ has been studied[294]. The condensation of two molecules of $Co_2(CO)_8$ to give $Co_4(CO)_{12}$ is an endothermic reaction but is entropy favoured. It was noted that rates of gas flow (in this case argon) and stirring efficiency can have a marked effect on measured rates of formation of $Co_4(CO)_{12}$. A small amount of EtOH surprisingly enhanced the formation of $Co_4(CO)_{12}$ although D.M.F. and T.H.F. do not have the same effect. Tying up all the loose ends and available information, the authors concluded that the mechanism for interconversion

of $Co_2(CO)_8$ to $Co_4(CO)_{12}$ is not as simple as previously supposed[132c], supporting this view by six points:

a) The difference between apparent (from concentration versus time plots) and true (from concentration dependence of initial rates) reaction orders.

b) The differences of reaction rates.

c) Variations in activation energies, depending on reaction conditions.

d) The non-ideal behaviour of the reaction at very low and very high conversions.

e) Influence of $h\nu$ on reaction rates.

f) Influence of alcohols on the reaction rates.

The alcohol catalysis, thermal and photochemical reactions could be explained by the type of mechanism outlined below in Fig. 5.4.

$$Co_2(CO)_8 \rightleftharpoons [Co(CO)_4]^+ + [Co(CO)_4]^-$$

$$H^+ + [Co(CO)_4]^- \rightleftharpoons HCo(CO)_4$$

$$HCo(CO)_4 + Co_2(CO)_8 \rightleftharpoons HCo_3(CO)_{10} + 2CO$$

$$2HCo_3(CO)_{10} \rightleftharpoons Co_4(CO)_{12} + 2HCo(CO)_4$$

Figure 5.4

However the function of $HCo(CO)_4$ requires a non ionic path e.g.

$$Co_2(CO)_8 \rightleftharpoons 2\,{}^{\bullet}Co(CO)_4 \qquad (5.10)$$

$${}^{\bullet}Co(CO)_4 + R\text{-}H \rightleftharpoons HCo(CO)_4 + {}^{\bullet}R \qquad (5.11)$$

where R = alkyl.

But the H abstraction step could be replaced by a radical reaction:

$${}^{\bullet}Co(CO)_4 + Co_2(CO)_8 \rightleftharpoons {}^{\bullet}Co_3(CO)_{10} + 2CO \qquad (5.12)$$

$${}^{\bullet}Co_3(CO)_{10} + Co_2(CO)_8 \rightleftharpoons Co_4(CO)_{12} + {}^{\bullet}Co(CO)_4 + 2CO \qquad (5.13)$$

The authors did not believe that two $Co_2(CO)_6$ fragments would react to give $Co_4(CO)_{12}$, being improbable that two fourteen electron species could live long enough to enable reaction. They did not rule out the interaction of $Co_2(CO)_6$ with $Co_2(CO)_8$ to produce $Co_4(CO)_{12}$ plus 2CO.

In summary they could not pinpoint the exact mechanism or mechanisms which operated, although for alcohol assisted reactions an ionic species for the disproportionation of $Co_2(CO)_8$ seemed likely.

This work, together with Chini et al.'s description of $[Co_4(CO)_{11}X]^-$ as an intermediate in the halide induced decomposition of $Co_4(CO)_{12}$ to $Co_2(CO)_8$[289], could explain a lot of confusing data on the kinetics of this interconversion.

To help simplify the kinetics of carbon monoxide substitution processes in $M_4(CO)_{12}$ clusters, Darensbourg and Incorvia have undertaken the investigation of phosphorus ligand substituted derivatives in hexane. The cluster $Co_4(CO)_{10}[P(OMe)_3]_2$ was found to proceed to $Co_4(CO)_9[P(OMe)_3]_3$ by a two term rate law (dissociative and ligand dependent paths) with the carbon monoxide dissociative process dominant at low incoming ligand concentrations[295]. However the substitution of $Co_4(CO)_{11}[P(OMe)_3]$ to give $Co_4(CO)_{10}[P(OMe)_3]_2$ was found to be strongly dependent on the concentration of the ligand, thereby obscuring any information on a possible carbon monoxide dissociative mechanism. Later they established that ^{13}CO incorporation into $Co_4(CO)_{12}$ is much slower than Ph_3P substitution[296], and that <u>substantial</u> rate enhancement for carbon monoxide dissociation was not evident with progressive phosphite substitution i.e.

$$Co_4(CO)_{12} \xrightarrow{1} Co_4(CO)_{11}[P(OMe)_3] \xrightarrow{1.7} Co_4(CO)_{10}[P(OMe)_3]_2 \xrightarrow{3.9} Co_4(CO)_9[P(OMe)_3]_3$$

No structural change occurs upon the introduction of the first substituent in contrast to the $Ir_4(CO)_{12}$ system.

A brief mention should be made in passing to the catalytic activity of $Co_4(CO)_{12}$. This species has been used in both hydroformylation and hydroesterification reactions. It has been noted that entry into the

catalytic cycle, via $HCo(CO)_3$, is easier with $Co_4(CO)_{12}$ than with $Co_2(CO)_8$ and so the former is the more active catalyst [297]. This reaction was investigated in the light of the assertion of Bor et al. that $Co_4(CO)_{12}$ conversion to $Co_2(CO)_8$ is slow, even at high pressures of carbon monoxide[292]. Using $Co_4(CO)_{12}$ or $Co_2(CO)_8$ hardly affected the isomeric distribution of the hydroformylation products, although in hydroesterification isomerisation is faster with $Co_4(CO)_{12}$ at temperatures above 100°C. The mechanism proposed for this work is shown in Fig. 5.5.

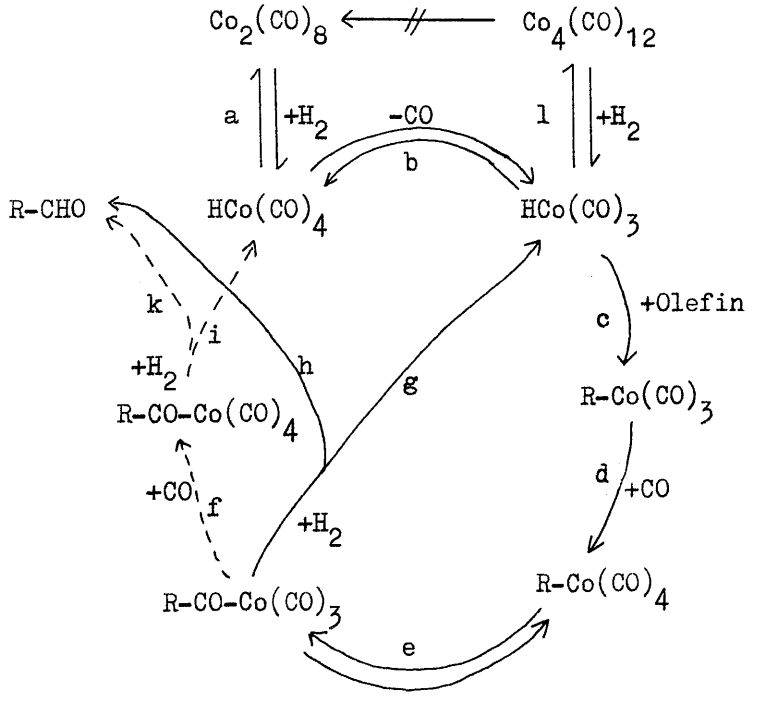


Figure 5.5

Reactions (a) and (b) were relatively slow and so not all of $Co_2(CO)_8$ was transformed into the active complex, e.g. $HCo(CO)_3$, whereas $Co_4(CO)_{12}$ can add molecular hydrogen to give $HCo(CO)_3$ directly, by path 1, with a lower activation barrier than required for steps (a) + (b), explaining the greater catalytic behaviour of $Co_4(CO)_{12}$.

The main catalytic cycle is path c, d, e, f and g while h and i are side-tracks. Since as time passes more of the catalyst ends up as

$RCOCo(CO)_4$, $HCo(CO)_4$ or $Co_2(CO)_8$ by various routes, the reactions of $Co_4(CO)_{12}$ and $Co_2(CO)_8$ become more equivalent. Also at higher temperature the difference between the two catalysts is reduced since $Co_2(CO)_8$ is more easily activated. The authors thought that hydroesterification would occur along the same lines using MeOH instead of hydrogen but side reactions e.g. disproportionation by the alcohol would intervene and there was not enough data to give a detailed discussion.

Part of the remainder of this chapter will be devoted to the effect of mixing different ratios of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ on the i.r. spectrum, with a view to explain some of the mysterious goings-on in the terminal carbonyl region. The effect of Co^{2+} and of $[Co(CO)_4]^-$ on $Co_4(CO)_{12}$ will also fall under the scope of this chapter in a bid to understand the complicated $Co_2(CO)_8$ reaction experienced in diethyl ether.

2. PREPARATION AND REACTIONS OF $Co_4(CO)_{12}$ IN ETHEREAL SOLVENTS.

$Co_4(CO)_{12}$ was prepared by refluxing $Co_2(CO)_8$ for 20 - 24 hours at 55 - 60°C in hexane, under nitrogen. The experimental set-up is shown in Fig. 5.6 with the gas inlet and outlet lines as described previously (chapter 2).

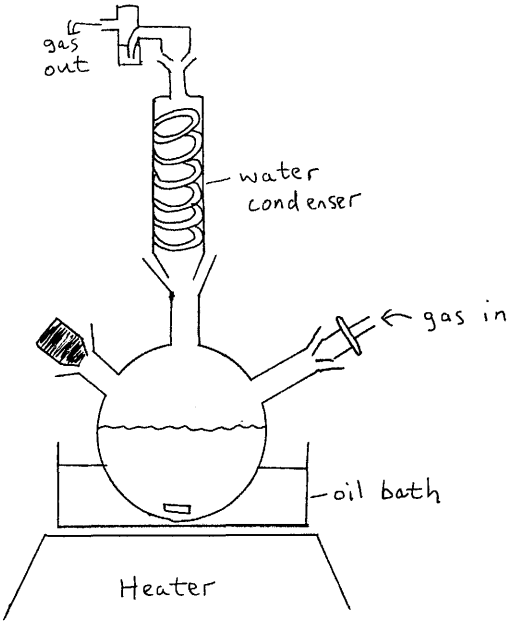


Figure 5.6

Frequently the $Co_2(CO)_8$ used had already started to decompose, and was considered unfit for any further experiments; thus completing the conversion to $Co_4(CO)_{12}$ was a convenient method of prolonging the material's usage.

The i.r. spectrum of $Co_4(CO)_{12}$ in hexane, T.H.F. (both run using the expanded scale of the P.E.257 spectrometer) and in diethyl ether is shown in Fig. 5.7

The effect of solvent (T.H.F.) and atmosphere (carbon monoxide and nitrogen) on $Co_4(CO)_{12}$ were then tested. Under carbon monoxide there is disappearence of the i.r. signals of the starting material, gradually being replaced by a very small amount of $Co_2(CO)_8$ and traces of $[Co(CO)_4]^-$ over a period of six hours. These i.r. spectra, shown in Fig. 5.8, were run on the P.E. 257 spectrometer.

Under nitrogen, there is still evidence of a considerable amount of $Co_4(CO)_{12}$ left after one day, with $[Co(CO)_4]^-$ also present in large amounts, see Fig. 5.9.

Next some Co^{2+}, in the form $Co(BF_4)_2$ / T.H.F., was added to a T.H.F. solution of $Co_4(CO)_{12}$ firstly under carbon monoxide, then under nitrogen. Over a period of five hours under carbon monoxide, no evidence of reaction was visible (Fig. 5.10a) but overnight some conversion to $[Co_3(CO)_{10}]^-$ (?), $Co_2(CO)_7$(T.H.F.), and $Co_2(CO)_8$ had occurred with no $Co_4(CO)_{12}$ present (Fig. 5.10b). These i.r. spectra were run on the P.E. 257 spectrometer. The signals assigned to $[Co_3(CO)_{10}]^-$ seem high for this species in T.H.F. Possibly there is coordination of BF_3 (from $[BF_4]^-$) to the oxygen of a bridging carbonyl group of $[Co_3(CO)_{10}]^-$, c.f. Li^+. As BF_3 is a better Lewis acid that Li^+ it will coordinate stronger and so shift the i.r. absorptions to higher frequency.

Under nitrogen, again there is no evidence of reaction after three hours

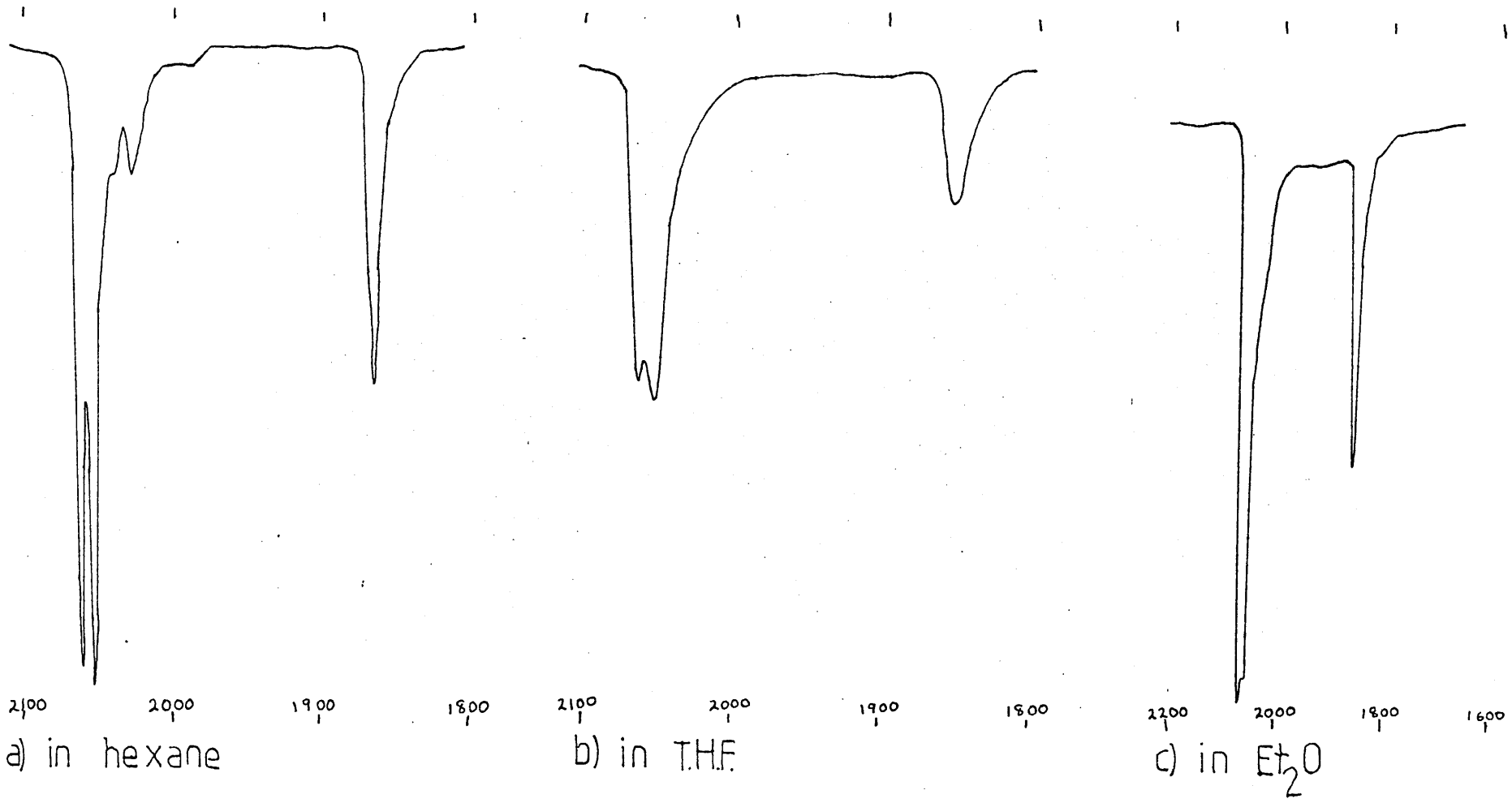
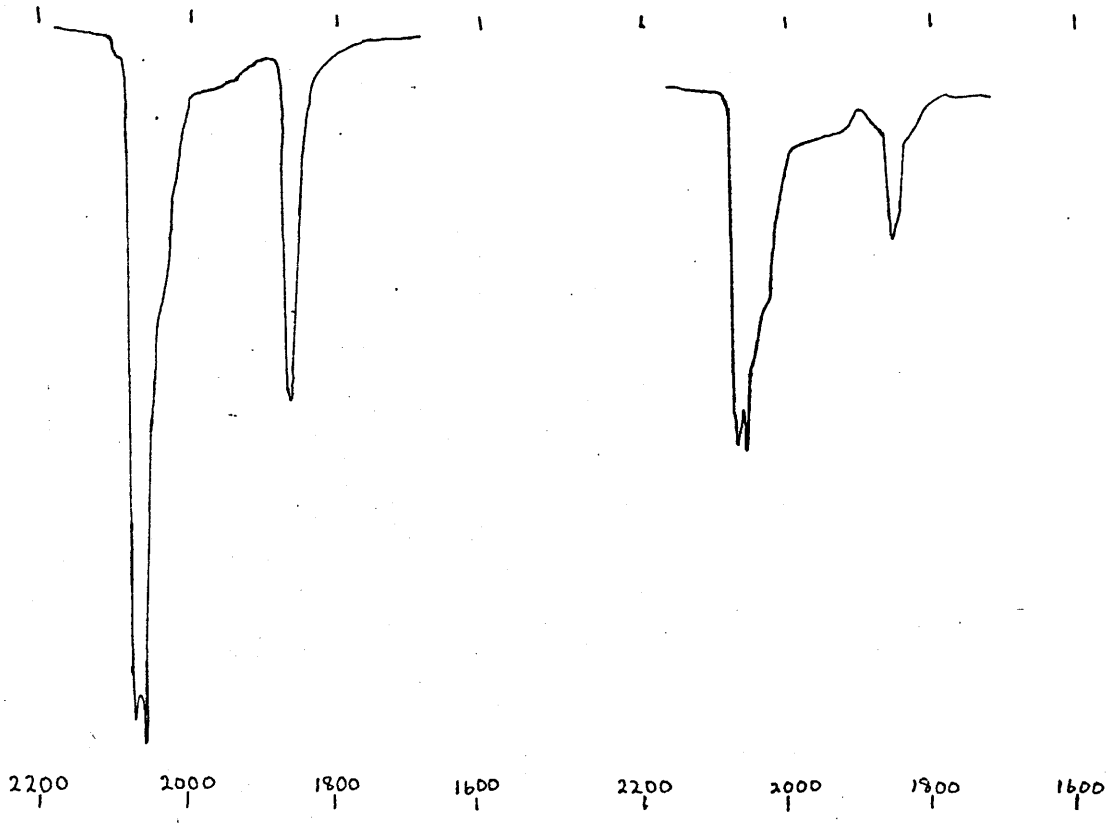
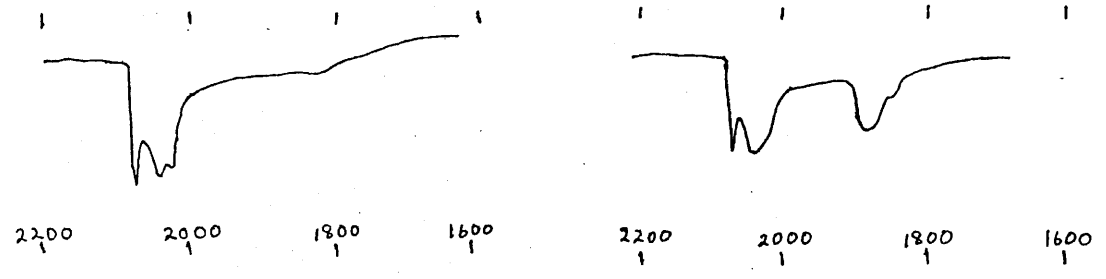

2100
2000
1900
1800
a) in hexane
2100
2000
1900
1800
b) in T.H.F.
2200
2000
1800
1600
c) in Et_2O

Figure 5.7



a) after 5mins

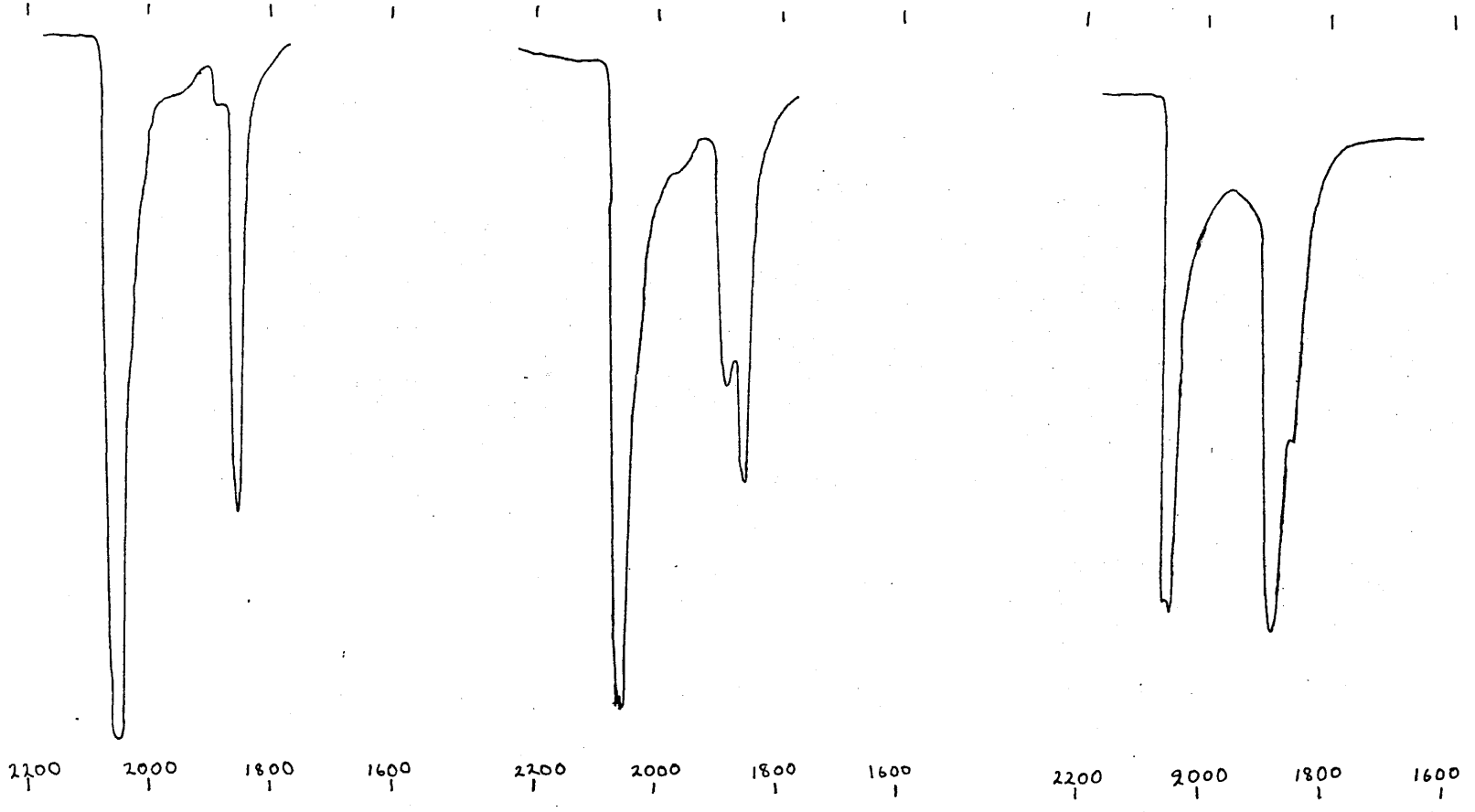
b) after 35mins



c) after 3hrs

d) after 6hrs

Figure 5.8



a) after 3mins b) after 55mins c) after 22hrs

Figure 5.9

Fig. 5.10c; overnight a mixture of $[Co(CO)_4]^-$ and $Co_2(CO)_7$ (T.H.F.) was formed - Fig. 5.10d.

Using $Co(SO_3Me)$ in T.H.F. instead, and under nitrogen, led to formation of $[Co(CO)_4]^-$, plus $Co_4(CO)_{12}$, after one and a half hours, with the former predominating after five and a half hours.

Our attention was then turned to the reaction of $Co_4(CO)_{12}$ and $Ph_4PCo(CO)_4$ under both atmospheres. Again only T.H.F. was used, since the latter reagent is insoluble in diethyl ether. Under carbon monoxide the initial i.r. spectrum obtained is shown in Fig. 5.12a. Over the next four hours slow consumption of $Co_4(CO)_{12}$ occurred, realising $Co_2(CO)_8$. The actual anion concentration did not change much overall. Using nitrogen as the atmosphere, there were signs of another species, $[Co_3(CO)_{10}]^-$ (?), after three minutes (Fig. 5.13a) as well as $Co_4(CO)_{12}$ and $[Co(CO)_4]^-$. Again slow disappearence of $Co_4(CO)_{12}$ from solution and growth of the $[Co_3(CO)_{10}]^-$ signal was noted over the next four and a half hours as shown by Fig. 5.13b and c. Overnight the $[Co(CO)_4]^-$ concentration became dominant with a signal above $2000cm^{-1}$, not $[Co_3(CO)_{10}]^-$. The reaction conditions described are ideal for cluster formations and so this signal is assigned to some unknown cobalt carbonyl cluster (Fig. 5.13d).

Finally, a series of i.r. spectra were recorded using different concentrations of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ in both T.H.F. and diethyl ether, under carbon monoxide. The benefit of this type of experiment was in showing the changes in, especially, the terminal carbonyl region caused by trace amounts of one or the other. There is no easier way of separating the overlapping bands of these two compounds in solution. The i.r. spectra of the T.H.F. solutions are shown in Fig. 5.14. For the diethyl ether experiments, two sets of i.r. spectra were recorded:

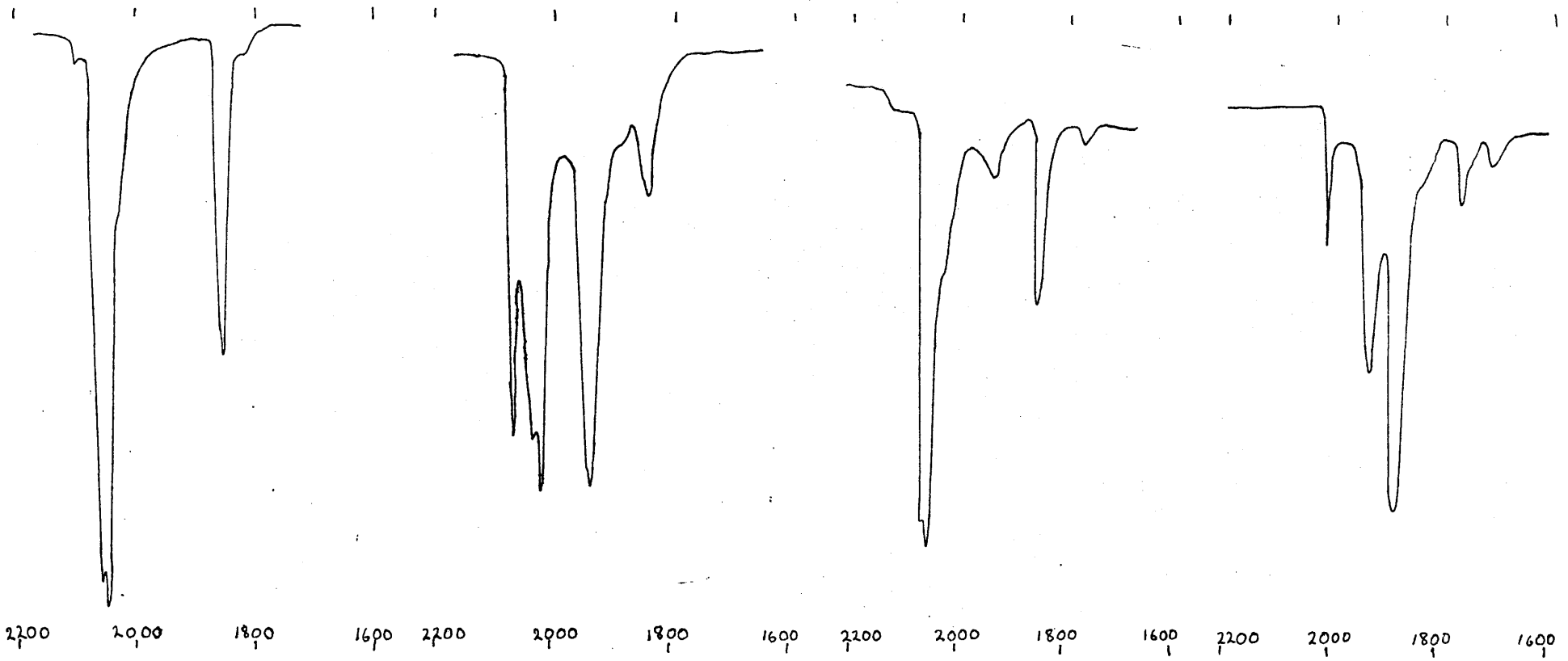
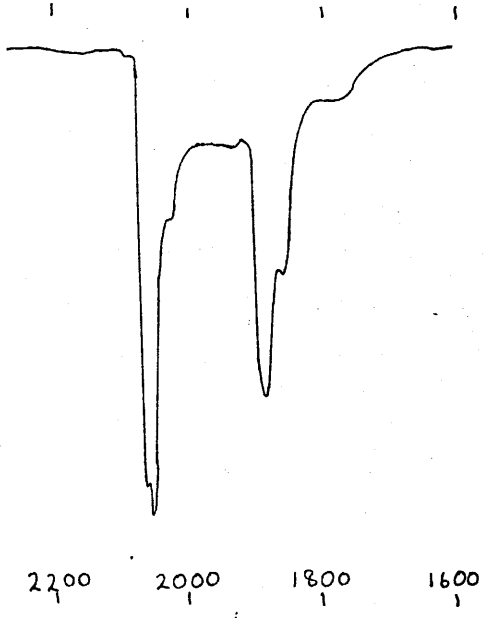
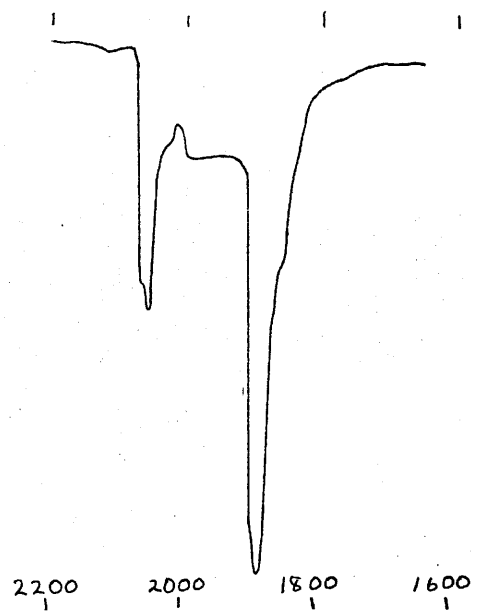


Figure 5.10 [see text]



a) after 1½ hrs



b) after 6hrs

Figure 5.11

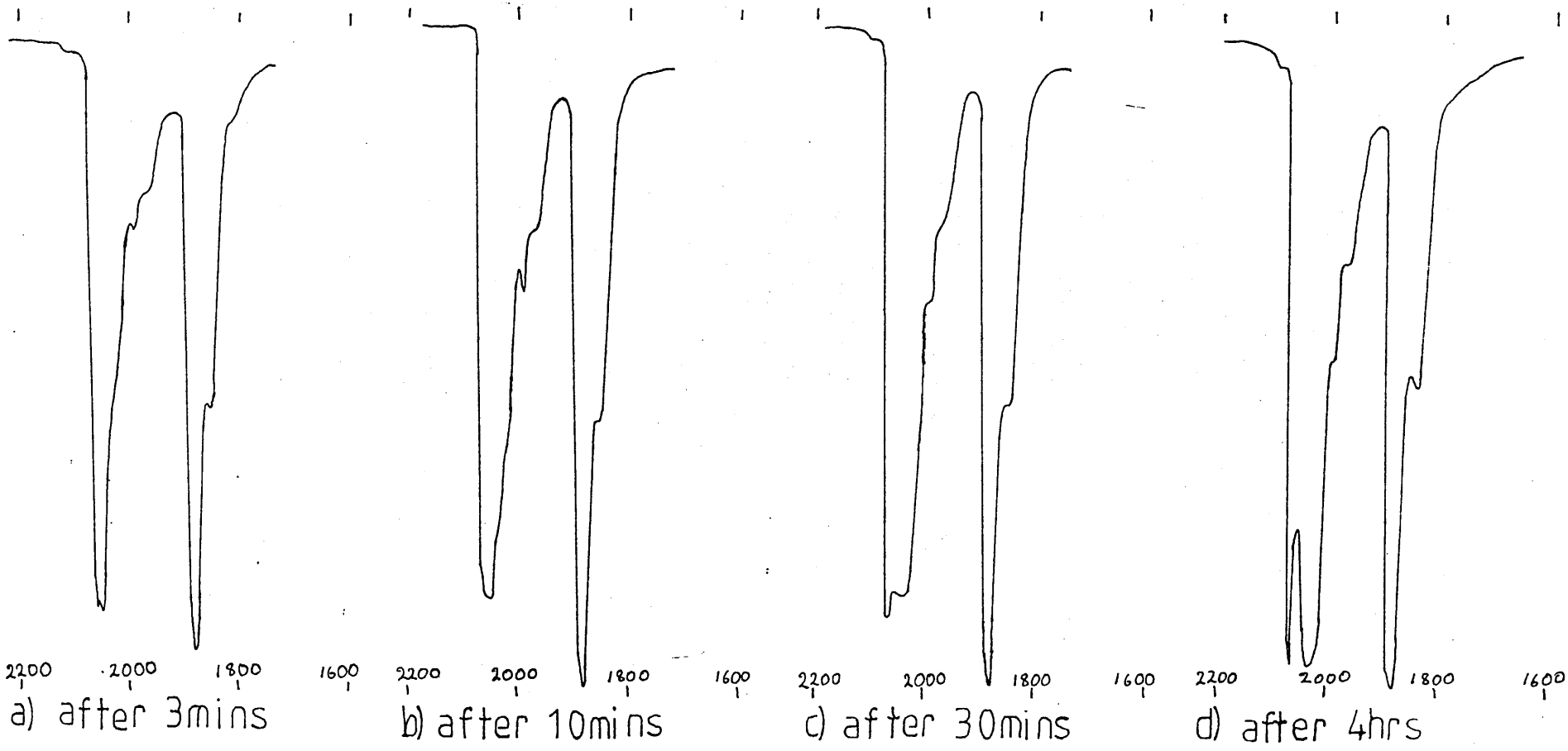

2200
2000
1800
1600
a) after 3mins
b) after 10mins
c) after 30mins
d) after 4hrs

Figure 5.12

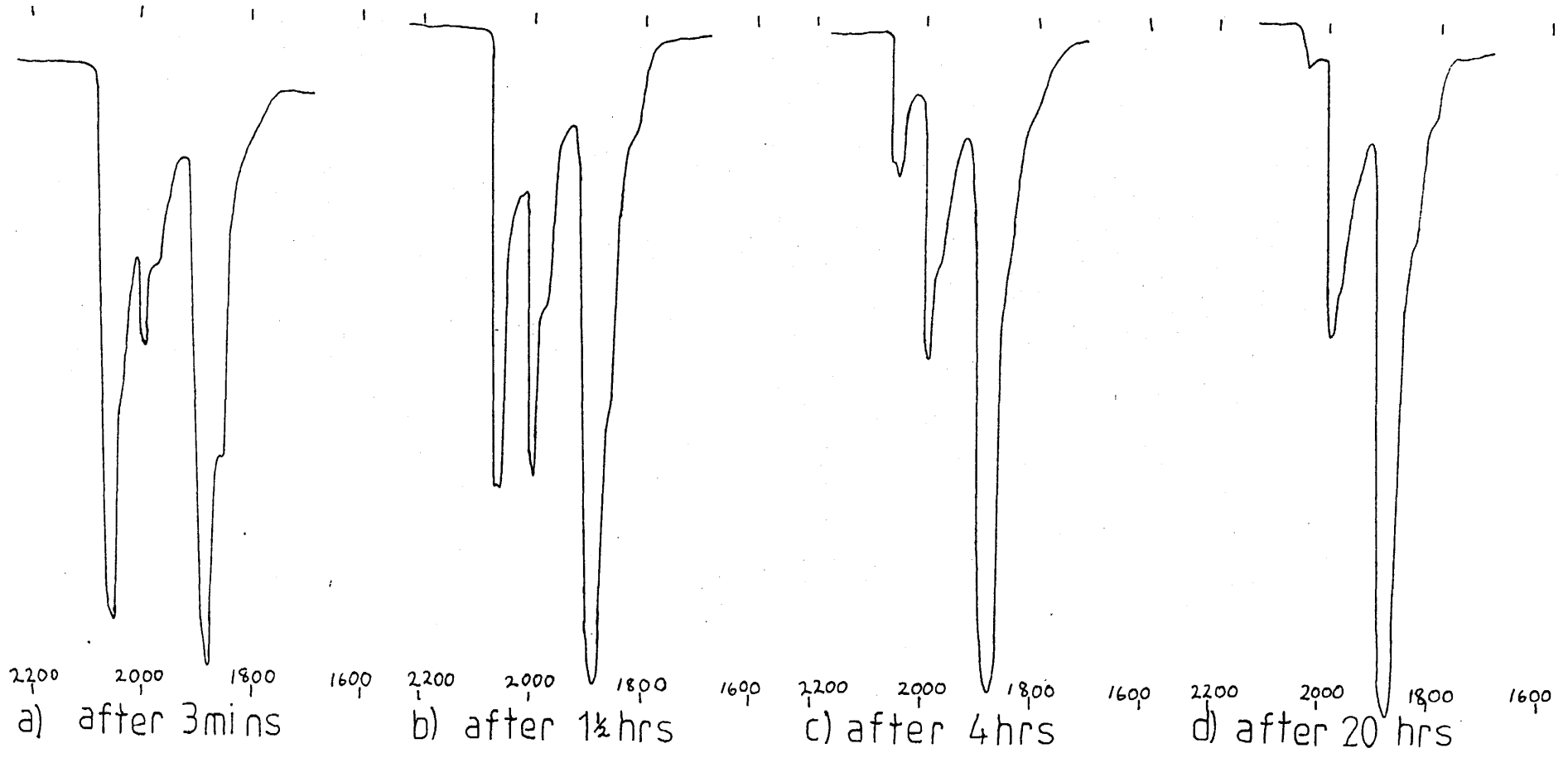

2200
2000
1800
1600
a) after 3mins
b) after 1½hrs
c) after 4hrs
d) after 20 hrs

Figure 5.13

1) ratio of $Co_2(CO)_8$: $Co_4(CO)_{12}$ concentration (as in T.H.F.),

2) ratio of the carbonyl concentration of $Co_2(CO)_8$: $Co_4(CO)_{12}$ i.e. keeping the total concentration of carbonyls in solution constant.

The spectra from the experiments using diethyl ether as the solvent are shown in Figs. 5.15 and 5.16.

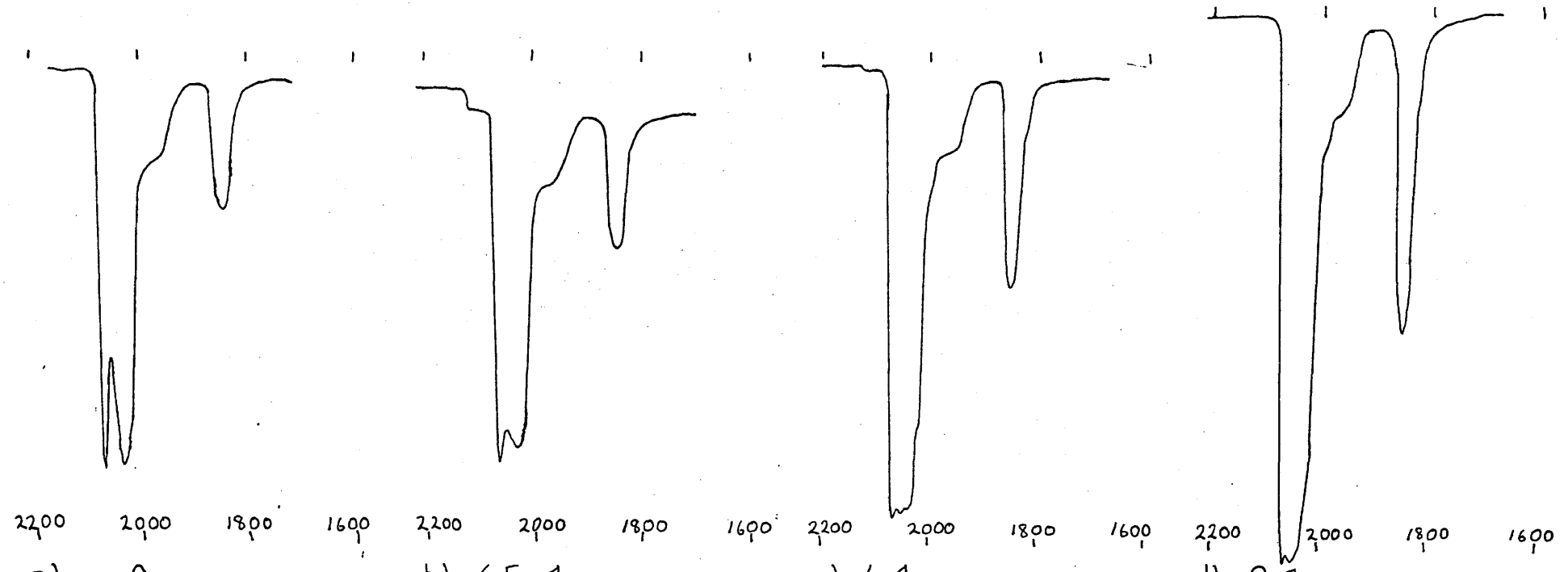
3. EXPERIMENTAL.

1. Preparation of $Co_4(CO)_{12}$

Typically 1.5 - 2.0g of $Co_2(CO)_8$ [4.39 - 5.85 x 10^{-3} moles] along with 100 ml hexane was placed in a 250 ml, three necked, round bottomed flask equipped with a stirrer bar, gas inlet and outlet, and water cooled condenser, as shown in Fig. 5.6. This was stirred, under a very slow nitrogen sweep, at around 60°C for 20 - 24 hours. The source of heat and the condenser were removed and the solution filtered, under nitrogen, through dried, siliconised glass wool into a single necked round bottomed flask. About half of the solvent was then removed on a rotoevaporator. When the solution had cooled to room temperature, it was left in dry ice (-78°C) for two to four hours to crystallise the product from the solvent. The solvent was decanted, the black lustre crystals washed with pentane (which had been kept at -78°C) and dried under a nitrogen stream. Their purity was checked by i.r. spectroscopy. While not in use this compound was kept at -5°C in a refrigerator under a nitrogen atmosphere.

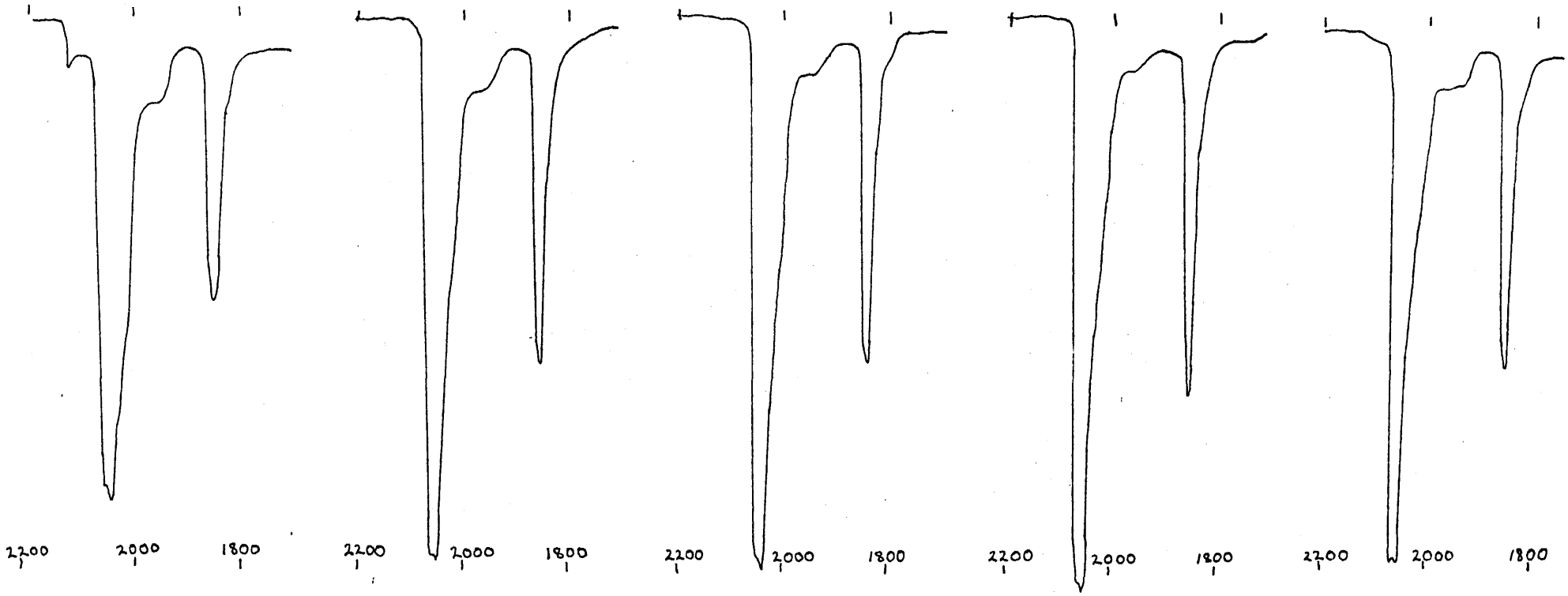
2. Preparation of $Co(SO_3Me)_2$ in T.H.F.

0.161g anhydrous $CoBr_2$ [7.36 x 10^{-4} moles] plus 0.247g $AgSO_3Me$ [1.22 x 10^{-3} moles] were placed in an oven dried single necked round bottomed flask, wrapped in aluminium foil. Previously both reagents had been dried for four hours at 40°C in vacuo. 10 ml freshly distilled T.H.F. was added, under nitrogen, and the mixture stirred for one hour in a sealed flask. The contents were then filtered through dried, siliconised glass wool, refiltered at the water pump through a sinter funnel,



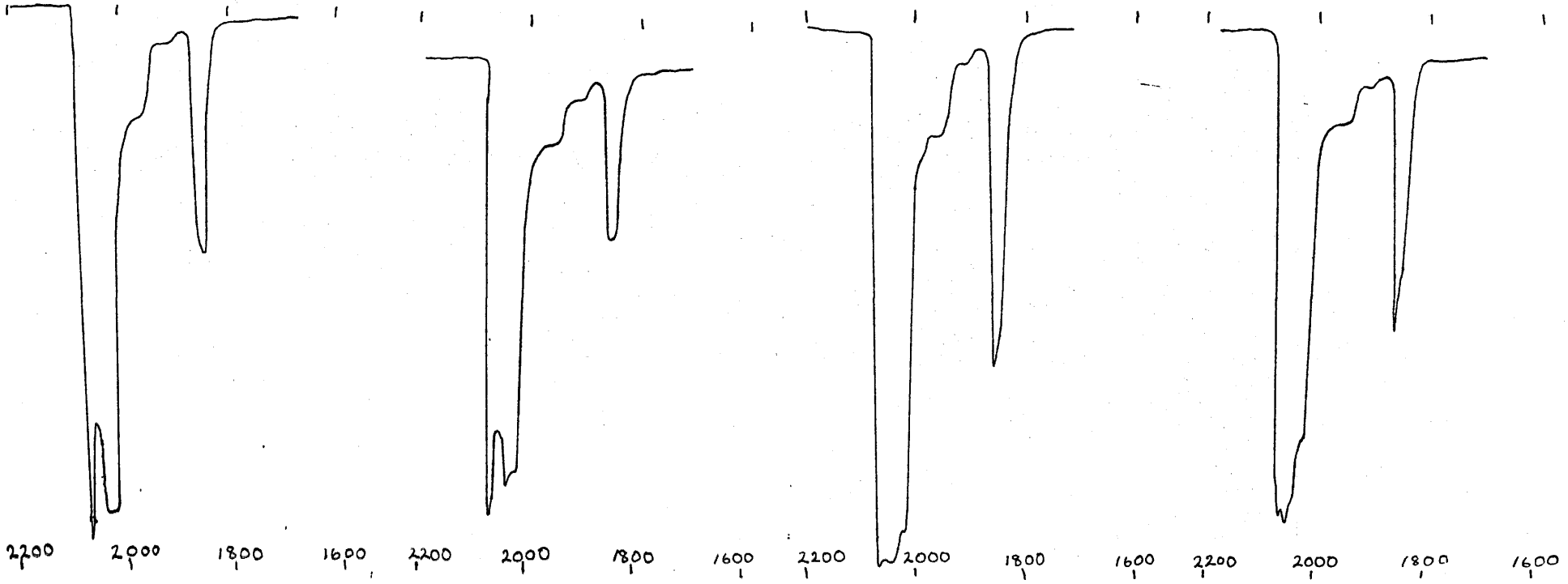
$Co_2(CO)_8$: $Co_4(CO)_{12}$ in T.H.F.

Figure 5.14



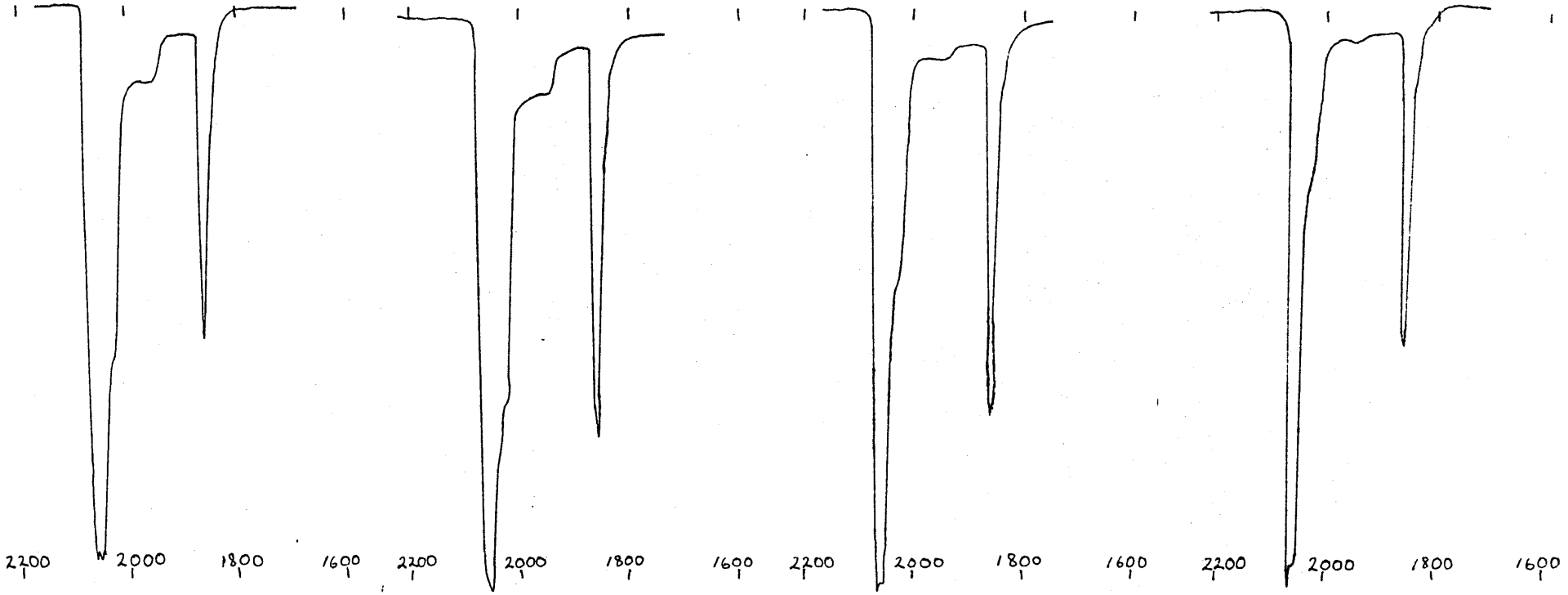
$Co_2(CO)_8$: $Co_4(CO)_{12}$ in T.H.F.

Figure 5.14[cont]



$Co_2(CO)_8$: $Co_4(CO)_{12}$ in Et_2O

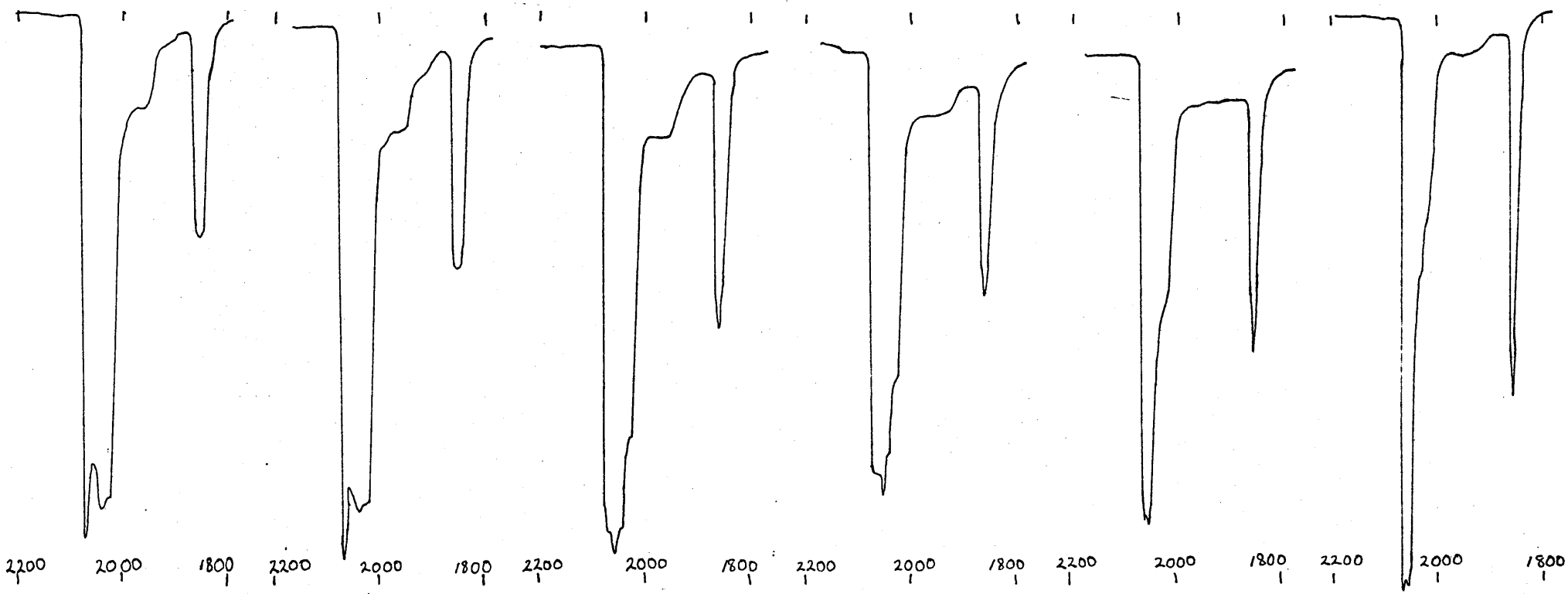
Figure 5.15



e) 1:1 f) 1 : 1.5 g) 1:4 h) 0 : ∞

$Co_2(CO)_8$: $Co_4(CO)_{12}$ in Et_2O

Figure 5.15[cont]



$Co_2(CO)_8$: $Co_4(CO)_{12}$ in Et_2O with CO concn. constant

Figure 5.16

to give a blue solution containing the product and a cream / grey solid, silver bromide. The filtrate was stored under nitrogen while not is use.

3. Reaction of $Co_4(CO)_{12}$ in T.H.F.

For all the experiments detailed in this section, the reaction set up described in chapter 2 was adopted. For the experiment involving $Co_4(CO)_{12}$ in T.H.F. under carbon monoxide, 0.15g $Co_4(CO)_{12}$ [2.62×10^{-4} moles] was added to 40 ml T.H.F; for the experiment under nitrogen, 0.28g $Co_4(CO)_{12}$ [4.50×10^{-4} moles] was used in 50 ml T.H.F. The solutions were stirred throughout under a slow gas stream and i.r. samples were removed by syringe through the septum cap. Both solutions were black / brown in colour.

The reaction of $Co_4(CO)_{12}$ and $Co(BF_4)_2$ in T.H.F., under carbon monoxide, required 0.20g $Co_4(CO)_{12}$ [3.50×10^{-4} moles] and 3ml $Co(BF_4)_2$ / T.H.F. solution, giving a brown coloured mixture which gradually lightened in colour while producing a fine suspension of greyish material. Under nitrogen similar colour changes were observed.

Using 3 ml $Co(SO_3Me)_2$ / T.H.F. with 0.15g $Co_4(CO)_{12}$ [2.62×10^{-4} moles] in 50 ml T.H.F., under nitrogen, also gave a brown solution.

For the experiments between $Co_4(CO)_{12}$ and $[Co(CO)_4]^-$, 0.299g $Co_4(CO)_{12}$ [5.23×10^{-4} moles] and 0.2549g $Ph_4PCo(CO)_4$ [4.99×10^{-4} moles] were used in 40 ml T.H.F. This gave an intense black solution becoming dark green / black overnight when under nitrogen but a brown solution under carbon monoxide. The blank experiment of $Co_4(CO)_{12}$ in T.H.F., under nitrogen, remained black / brown throughout. In the experiments under nitrogen, the blank experiment and the reaction involving $[Co(CO)_4]^-$ were connected, as illustrated in Fig. 5.17. This was to establish that no impurities or side reactions of nitrogen were responsible for reactions in the main experiment.

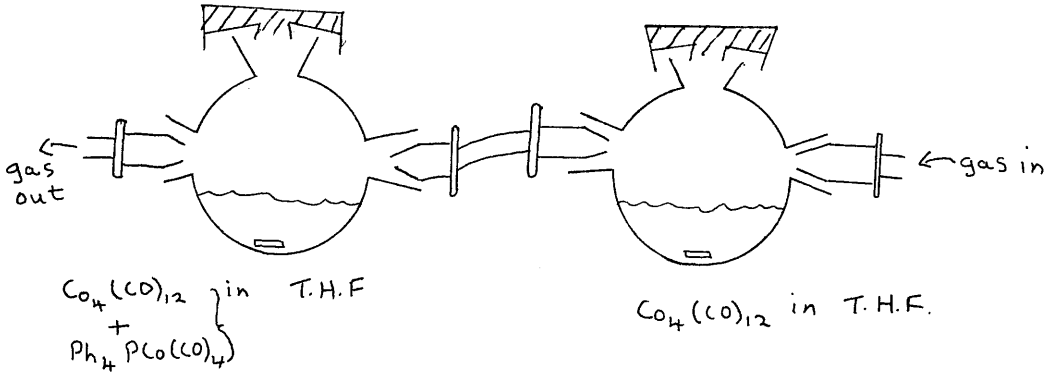


Figure 5.17

4. Interaction of $Co_4(CO)_{12}$ and $Co_2(CO)_8$ in Ethereal Solvents

All the experiments, in both diethyl ether and T.H.F., were carried out in an identical manner, as detailed below.

An oven dried, 10 ml conical flask fitted with a B14 stopper was purged with a strong carbon monoxide flow then stoppered. Into this was weighed the requisite amount of $Co_4(CO)_{12}$ first, then $Co_2(CO)_8$. The latter is the more air sensitive compound and so is added second. 1.5 ml of the required solvent was syringed in, the flask shaken for half a minute, then a sample removed for i.r. inspection. The flask was washed out with EtOH and dried in the oven before re-use, while the i.r. sample cell was cleaned using the solvent of the experiment. Care was exercised in minimising the loss of the carbon monoxide atmosphere from the flask during weighings.

For ease of reference, the weight and calculated number of moles of each compound and the effective ratios of them are detailed in the tables below. Table 2 is for the experiment in T.H.F., table 3 is for the same experiment in diethyl ether, where the overall total number of moles of reactants was kept constant, and table 4 is the experiment in diethyl ether where the total number of moles of carbonyl was kept constant. This step was taken to solve the problem of i.r. spectra being too intense.

TABLE 5.2

Fig. 5.14	Wt. $Co_2(CO)_8$ $x10^{-3}g$	Wt. $Co_4(CO)_{12}$ $x10^{-3}g$	Moles $Co_2(CO)_8$ $x10^{-5}$	Moles $Co_4(CO)_{12}$ $x10^{-5}$	Ratio (of moles)
a	10.0	-	2.92	-	∞ :0
b	9.3	2.8	2.72	0.49	6.41:1
c	9.0	3.7	2.63	0.65	4.07:1
d	8.0	5.7	2.34	1.00	2.34:1
e	5.6	8.6	1.64	1.50	1.09:1
f	3.6	12.0	1.05	2.10	1:1.99
g	2.2	14.1	0.64	2.47	1:3.83
h	1.1	15.6	0.32	2.73	1:8.48
i	-	11.4	-	1.99	0: ∞

TABLE 5.3

Fig. 5.15	Wt. $Co_2(CO)_8$ $x10^{-3}g$	Wt. $Co_4(CO)_{12}$ $x10^{-3}g$	Moles $Co_2(CO)_8$ $x10^{-5}$	Moles $Co_4(CO)_{12}$ $x10^{-5}$	Ratio (of moles)
a	15.0	-	4.39	-	∞ :0
b	9.0	1.8	2.63	0.32	8.36:1
c	8.1	3.4	2.37	0.60	3.98:1
d	7.0	5.7	2.05	1.00	2.05:1
e	5.3	8.5	1.55	1.49	1.04:1
f	4.3	11.1	1.26	1.94	1:1.54
g	2.2	13.6	0.64	2.38	1:3.70
-	Omitted since Fig. 5.15g showed $Co_4(CO)_{12}$ to dominate				
h	-	11.5	-	2.011	0: ∞

TABLE 5.4

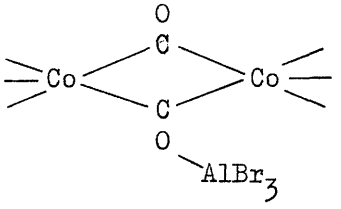
Fig. 5.16	Wt. $Co_2(CO)_8$ $x10^{-3}g$	Wt. $Co_4(CO)_{12}$ $x10^{-3}g$	Moles of CO in $Co_2(CO)_8$ $x10^{-5}$	Moles of CO in $Co_4(CO)_{12}$ $x10^{-5}$	Ratio (of moles of CO)
a	10.0	1.4	23.40	2.94	7.96:1
b	9.2	2.2	21.52	4.62	4.66:1
c	6.8	4.4	15.91	9.23	1.72:1
d	5.5	5.2	12.87	10.91	1.18:1
e	3.7	7.0	8.66	14.69	1:1.70
f	1.8	10.5	4.21	22.03	1:5.23

4. DISCUSSION

As noted in the literature, $Co_4(CO)_{12}$ under a carbon monoxide atmosphere gave $Co_2(CO)_8$[292]. Under nitrogen only $[Co(CO)_4]^-$ is found in addition to $Co_4(CO)_{12}$, this being a direct result of the polar solvent induced reaction[136]. No evidence of $Co_2(CO)_8$ was noted.

Co^{2+}, as the $[BF_4]^-$ salt, would appear to inhibit decay of $Co_4(CO)_{12}$ under carbon monoxide, taking far longer than the blank experiment to show signs of reaction and even then only the intermediate stages between $Co_4(CO)_{12}$ and $Co_2(CO)_8$, i.e. $[Co_3(CO)_{10}]^-$ and $Co_2(CO)_7$(T.H.F.), are observed. Under nitrogen a similar story unfolds, i.e. inhibition of the reaction towards $[Co(CO)_4]^-$ formation, although this does take place overnight. Co^{2+}, as the $[SO_3Me]^-$ salt, does not appear to differ very much from the rate of reaction exhibited by the blank experiment.

Adduct compounds of cobalt carbonyls are well known e.g. $[(PhCH_2)_4P][H_3BCo(CO)_4]$ has been made[198]; $Co_2(CO)_8AlBr_3$ has also been isolated and its structure determined by i.r. and Raman techniques to show an O-bonded adduct rather than a Co_2Al interaction, as originally proposed[298]. The $AlBr_3$ unit is attached at one of the bridging carbonyls i.e.



terminal carbonyls omitted for clarity

Figure 5.18

It was suggested that Co^{2+} can coordinate to a bridging carbonyl group of $Co_2(CO)_8$[299]; perhaps something of a similar nature is happening here with the bridging carbonyls of $Co_4(CO)_{12}$?

The reaction of $Co_4(CO)_{12}$ with $[Co(CO)_4]^-$ went very much as expected; where carbon monoxide abounds, there is total conversion to $Co_2(CO)_8$

and $[Co(CO)_4]^-$ but under nitrogen conversion to anion, with traces of $[Co_3(CO)_{10}]^-$ at the intermediate stage, occurs, c.f. the reaction of $Co_4(CO)_{12}$ alone in T.H.F. The presence of the anion only serves to increase the rate of reaction in both situations.

The results of mixing $Co_2(CO)_8$ and $Co_4(CO)_{12}$ in ethereal solvents were most enlightening. It solved the problems of "mysterious" i.r. spectra by showing just how much traces of one species, especially $Co_4(CO)_{12}$, could alter the terminal carbonyl region of the other. It also explained why the plots of absorption versus time, shown in earlier chapters, did not help a great deal; under circumstances where absorptions from more than one species in solution overlap, it is well nigh impossible, with our limited facilities, to resolve these bands and this renders any such plots useless. In these situations, the majority of assignments were made with hindsight after these experiments had been carried out.

Unfortunately not all of the abnormalities of the i.r. spectra were explained (see chapter 2), but it is now understood that only traces of some cobalt carbonyl deficient species can cause changes in the i.r. pattern and although this is worthy of investigation, it will have to be left until another time.

CHAPTER 6

MISCELLANEOUS

CHAPTER 6 - MISCELLANEOUS

This chapter completes the review of the work of this thesis. It collects together the few experiments which did not fit into any of the preceeding categories and will be in three parts - kinetics of disproportionation of $Co_2(CO)_8$, preparation and some reactions of $CoBr_2$, preparation, characterisation and some reactions of $Ph_4PCo(CO)_4$.

1. Kinetics of Disproportionation by n-Tetrabutylammonium Iodide.

Kinetics of substitution in, and reactions of, $Co_2(CO)_8$ have received much attention because of the importance of the intermediate complexes in catalytic reactions. One of the neater examples was published in 1963, by Bor and Marko, concerning the substitution of $Co_2(CO)_8$ by Ph_3P[230]. At this stage both $[Co(CO)_3(PR_3)_2]^+[Co(CO)_4]^-$ and $Co_2(CO)_6(PR_3)_2$ were both known but the monosubstituted derivative $Co_2(CO)_7(PR_3)$ was not. The experiment used the highly viscous nujol as a medium to slow down the reaction rates. By this method the solid compound illustrated in Fig. 6.1 was isolated. The structure was inferred from the i.r. data, in hexane: 2079w, 2026w, 2010sh, 1996vs and 1964w, cm^{-1}. This showed no bridging carbonyl groups but five bands in the terminal carbonyl region consistent with C_{3v} symmetry $(3A_1 + 2E)$.

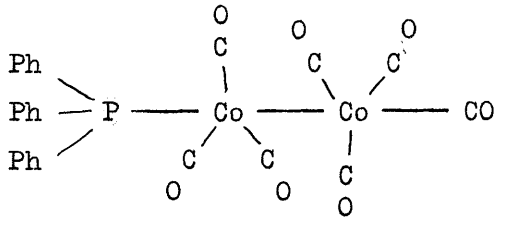


Figure 6.1

Reaction of $Co_2(CO)_7PPh_3$ with Ph_3P to give a mixture of the ionic salt and disubstituted compound, listed above, was proof of this compound being an intermediate stage in these reactions starting from $Co_2(CO)_8$.

Some kinetic work done in this department had shown that the reaction of $Co_2(CO)_8$ with n-Bu_4NI in toluene was first order w.r.t. the concentration of n-Bu_4NI[225]. From the present work, and from the results in the literature, the rates of reactions involved would appear to be as shown in Fig. 6.2:

$$Co_2(CO)_8 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co_2(CO)_7 + CO \xrightarrow[+R]{k_2} \text{products}$$

k_2 small, rate = $[R]\, k_2\, [Co_2(CO)_7] = k_2 RK \dfrac{[Co_2(CO)_8]}{[CO]}$

k_{-1} small, rate = $k_1\, [Co_2(CO)_8]$

assuming $[Co_2(CO)_7]$ to be small or steady.

Figure 6.2

To provide corroborative evidence for the above, a kinetic study of $Co_2(CO)_8$ and n-Bu_4NI in toluene and T.H.F. was undertaken. Since the reaction in T.H.F. is very fast, the experiments were to be conducted at 0^oC and so the first step was to investigate the reaction of $Co_2(CO)_8$ and Bu_4NI in toluene, at 0^oC, under carbon monoxide. This proved extremely difficult both in keeping the temperature constant and in persuading n-Bu_4NI to completely dissolve in toluene at 0^oC. This limited the collection of worthwhile kinetic data. Only reactions in toluene or T.H.F. at 25^oC, under both carbon monoxide and nitrogen gave informative results.

Experimental

For the experiments at 0^oC, a thermostat bath of ice / water was used; ice was also used in the hollow column of the cell holders to cool them to 0^oC. The normal experimental set-up, described in chapter 2, was used with the reaction vessels shaken by hand periodically instead of

using a stirrer bar. A stock solution of $Co_2(CO)_8$ in toluene, comprising 0.791g $Co_2(CO)_8$ [2.31×10^{-3} moles] in 120 ml dried toluene, was kept at -78°C when not being used, and only allowed to warm up to the required temperature immediately prior to transfer to the reaction vessels. 20 ml of such a solution was used in turn with 0.455g [1.23×10^{-3} moles], 0.889g [2.43×10^{-3} moles] and 0.919g [2.49×10^{-3} moles] n-Bu_4NI.

For the reactions at 25°C, in a thermostat bath, 20 ml of the same stock solution of $Co_2(CO)_8$ in toluene was used with 0.455g n-Bu_4NI [1.23×10^{-3} moles] under carbon monoxide. This was then repeated under nitrogen.

For the reactions in T.H.F. at 25°C, 0.227g Bu_4NI [6.15×10^{-4} moles] plus 0.120g $Co_2(CO)_8$ [3.51×10^{-4} moles] were placed in the reaction vessel, under nitrogen, and 10 ml T.H.F. syringed in, giving a green solution with gas evolution. The reaction was over in ten minutes.

Under carbon monoxide, 0.234g Bu_4NI [6.33×10^{-4} moles] and 0.121g $Co_2(CO)_8$ [3.54×10^{-4} moles] were used with 10 ml T.H.F. to give a green / brown solution, with the customary gas evolution initially until the reaction was complete after fifteen minutes and a green solution was present.

For the reactions involving a nitrogen gas flow, the reaction vessel was altered, as shown in Fig. 6.3. The gas frit incorporated in the bottom of the flask was to improve the ability of nitrogen to sweep out any carbon monoxide in solution, present as a result of disproportionation.

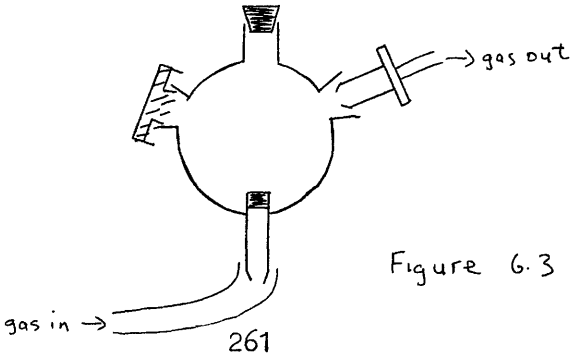


Figure 6.3

DISCUSSION

In both T.H.F. and toluene, addition of n-Bu_4NI increased the rate of disproportionation w.r.t. only $Co_2(CO)_8$ and solvent being present. In T.H.F., as expected, the reaction is much quicker, due to the role of the solvent in Lewis base attack on $Co_2(CO)_8$. Under carbon monoxide the reaction is slower than under nitrogen which lends support to the reaction scheme of Fig. 6.2 i.e. dissociation of $Co_2(CO)_8$ to $Co_2(CO)_7$ and CO (which is inhibited by a carbon monoxide atmosphere) is the first step of the disproportionation reaction. Reactions at 0^oC are very much slower than at 25^oC and there are problems re the solubility of n-Bu_4NI in toluene at this temperature.

Investigation of these reactions at 0^oC would be most rewarding in terms of understanding the roles of the solvent and the atmosphere in such reactions.

2. COBALT DIBROMIDE IN ETHEREAL SOLVENTS

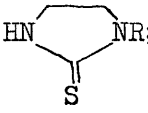
One of the earliest preparations of $CoBr_2$ was reported in 1914, the compound being isolated as the etherate[300]. The method was simple - cobalt metal plus bromine, in the correct stoichiometric ratio, added together in diethyl ether to give $CoBr_2Et_2O$ by analysis. This could be decomposed by heat to give the anhydrous $CoBr_2$ as a green powder. A more recent method was described where cobalt carbonate $CoCO_3$, and hydrobromic acid were reacted to give $CoBr_2 6H_2O$, then dehydration in vacuo at 130^oC followed to give the desired product[301].

Cobalt halides, CoX_2, are very easily hydrolysed to give the hexahydrate compound. In solutions it is not surprising that solvent molecules will, in the absence of water, coordinate to Co^{2+} to give similar solvent adducts. These can easily be followed by the colour changes e.g. anhydrous $CoBr_2$ is bright green, the hexahydrate is red / purple and the T.H.F. adduct is blue. The changes, which can be observed below

room temperature, can be interpreted in terms of octahedral - tetrahedral configurational changes of solvated Co^{2+} complexes and the spectral behaviour of such compounds has been studied.[302] This showed in general pink / red colours correlated with octahedral compounds and blue with tetrahedral compounds. For octahedral complexes the ^4F groundstate is split by the ligand field to give $^4A_{2g}$, $^4T_{2g}$, and $^4T_{ig}$, the latter becoming the new groundstate. Spin allowed transitions to $^4A_{2g}$, $^4T_{2g}$ and $^4T_{1g}$ can occur, the rest are forbidden. In the tetrahedral case, there are three spin allowed bands, two in the i.r. and the third in the red region of the spectrum, hence blue colours of such solutions[303].

Cobalt halides in solution tend to exist as Co^{2+} and $[CoX_4]^{2-}$ ions. Even in "inert" solvents these will interact to give complexes of the type $CoX_{4-n}S_n$, S = solvent[304].

The simple ethers have long been known to act as donors towards first row transition metals. In 1968 a paper discussing dioxanates of metal halides, under anhydrous conditions, was published[305]. Previously such compounds were prepared using anhydrous reagents and conditions. Here the hydrated metal halides and 1,4 dioxan were mixed in the presence of a sufficient excess of triethyl orthoformate which chemically removes water from the system. The $CoX_2.C_4H_8O_2$ system, X = Cl or Br, were shown to be octahedral species by magnetic moment and far i.r. considerations.

However using N-monosubstituted 1,3 imidazolidines - 2 - thione with CoX_2(X = Cl, Br or I) give $Co_2L_2X_2$ complexes with L being S bonded to cobalt[306] [L =  ; R = Me, Et].

The colour (blue to green), magnetism and electronic spectra of these compounds indicate a tetrahedral stereochemistry with C_{2v} local symmetry.

T.H.F. solutions of M^{2+} compounds are numerous.

$[Co(T.H.F.)_6][SbCl_6]_2$ which is light purple in colour has been made as part of a series of M^{2+} salts making Co^{2+} octahedrally surrounded by 6 oxygen atoms[307]. This demonstrates the use of ethers as ligands. Macrocyclic ligands have been used in stabilising M^{2+} centres e.g. potentially pentadentate ligands have been used to give five coordinate Co^{2+} attached to ether oxygen in the solid state[308]. Similarly chelating ligands have been used to give five coordinate Co^{2+} [309a] or six coordinate Co^{2+} [309b]. More recently bipyridyl hexaethyleneglycol crown ether was reported to react with $CoCl_2$ to give a pentacoordinate complex containing a "novel" Co^{II} - O (ether) bond in the solid state[310]. This claim to novelty was disputed, and certainly appears to be slightly exaggerated in view of the aforementioned evidence[311]. Further support for the lack of novelty of this type of bond has come from W.L. Driessen, when discussing Co(II) - ether bonding[312].

In an attempt to isolate solid etherates of $CoBr_2$, two different methods were used for both diethyl ether and T.H.F. compounds. Firstly using cobalt metal and bromine in diethyl ether, a green solid was isolated using a nitrogen flow to blow off excess solvent. The compound readily decomposed in the atmosphere and no satisfactory analytical data were obtained. For the T.H.F. adduct, a green solution with a pale green precipitate was the initial result but under a nitrogen flow a pale blue solid was formed. On redissolving this in T.H.F. a green solution and solid resulted.

These results did not seem to be very accurate and so the other method of making the etherates was employed. Anhydrous $CoBr_2$, in a flask connected to the vacuum line, had freshly dried T.H.F. distilled onto it resulting in a kingfisher blue coloured solution. Under a nitrogen atmosphere, this yielded a blue solid and solution over a few days. Careful isolation of this solid followed; any exposure to moisture

resulted in the purple colouration of the hexahydrate.

The visible / U.V. spectrum of the solid, as a KBr disc obtained and is shown in Fig. 6.4a Similar results were given by a nujol mull of the compound and the solution spectrum is shown in Fig. 6.4b, along with that of the compound made by the first route (Fig. 6.4c). The solution spectra in this section were recorded on the Pye Unicom SP8-100 spectrometer, unless stated to the contrary.

The i.r. spectrum of the solid, as a KBr disc, was recorded but proved unhelpful since any vibrations due to $CoBr_2$ are at low frequencies, outwith the range of the machine.

Adding a few drops of water to both solutions (i.e. of the compounds isolated by each route) led to the near total collapse of the solution visible / U.V. spectra with the solutions becoming pale pink in colour. Drying these solutions over $MgSO_4$ reversed this, giving spectra similar to those initially obtained.

By comparison to literature work, these spectra show that when dry, the sample prepared by the second method has Co^{2+} tetrahedrally coordinated while the first method gave tetrahedral and octahedral coordination of Co^{2+}.

The preparation of a $CoBr_2$ - T.H.F. solution was carried out, the solution being decanted directly into a visible / U.V. cell and the spectrum (against T.H.F.) in both visible / U.V. and near i.r. regions recorded. (Fig. 6.5 a & b). The spectrometer used was the Beckman 5270.

To see how many molecules of T.H.F. were present in the solid $CoBr_2$ sample, some of the compound was sent for elemental analysis. Unfortunately decomposition had occured before the results were finalised. Similar attempts to determine the melting point of such derivatives met with failure. On heating to $28^{o}C$ in air, any T.H.F. in the compound was lost from the sample and the purple hexahydrate was formed; water was

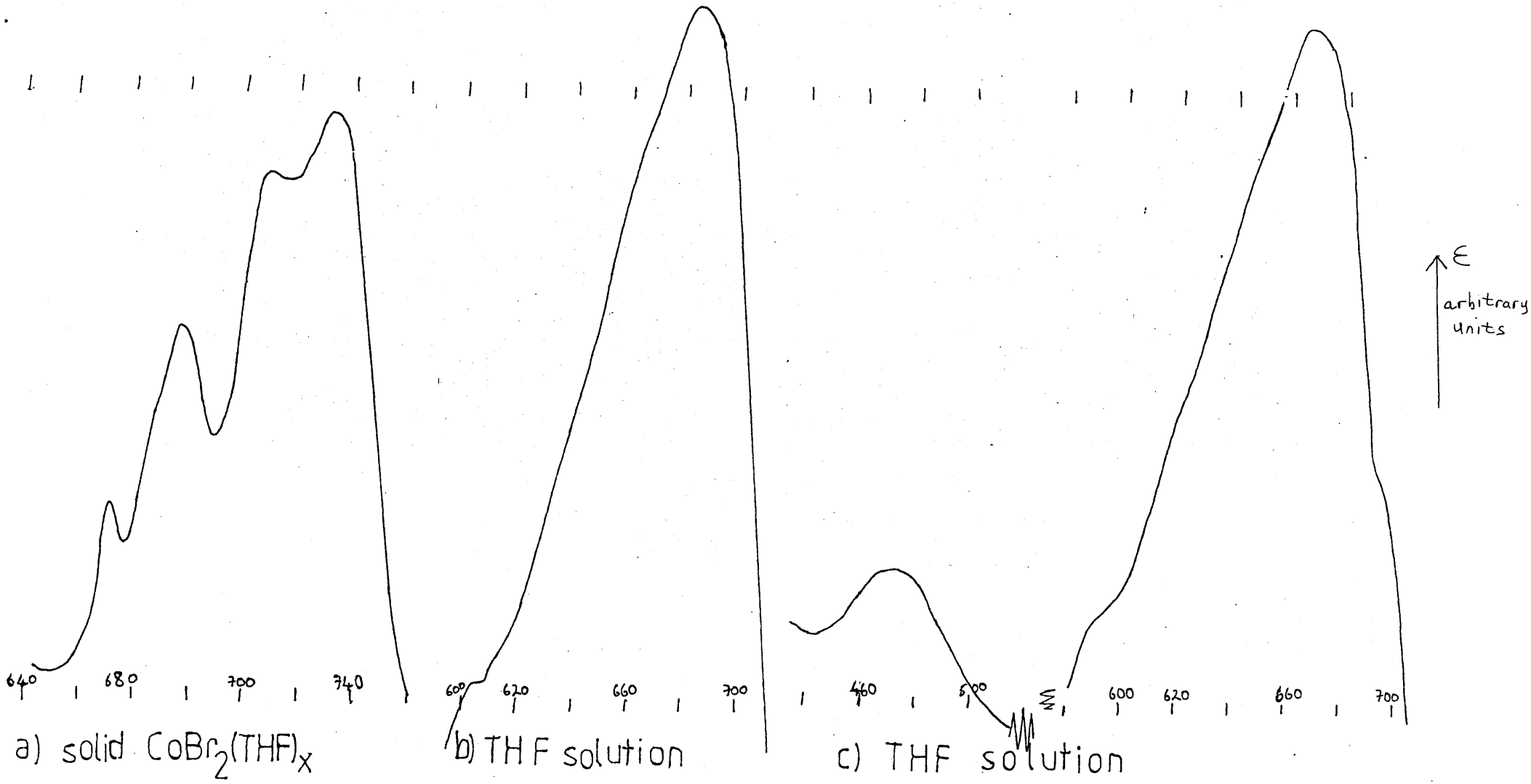
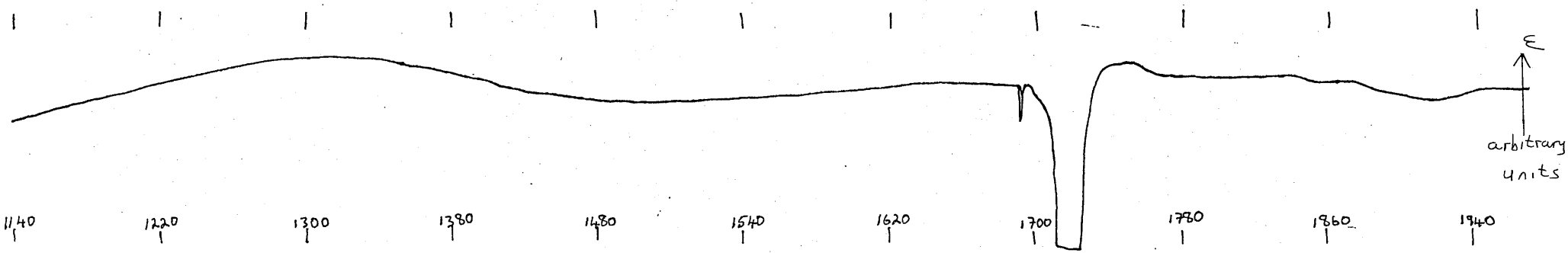


Figure 6.4 [see text]


ε
arbitrary units
1140
1220
1300
1380
1480
1540
1620
1700
1780
1860
1940

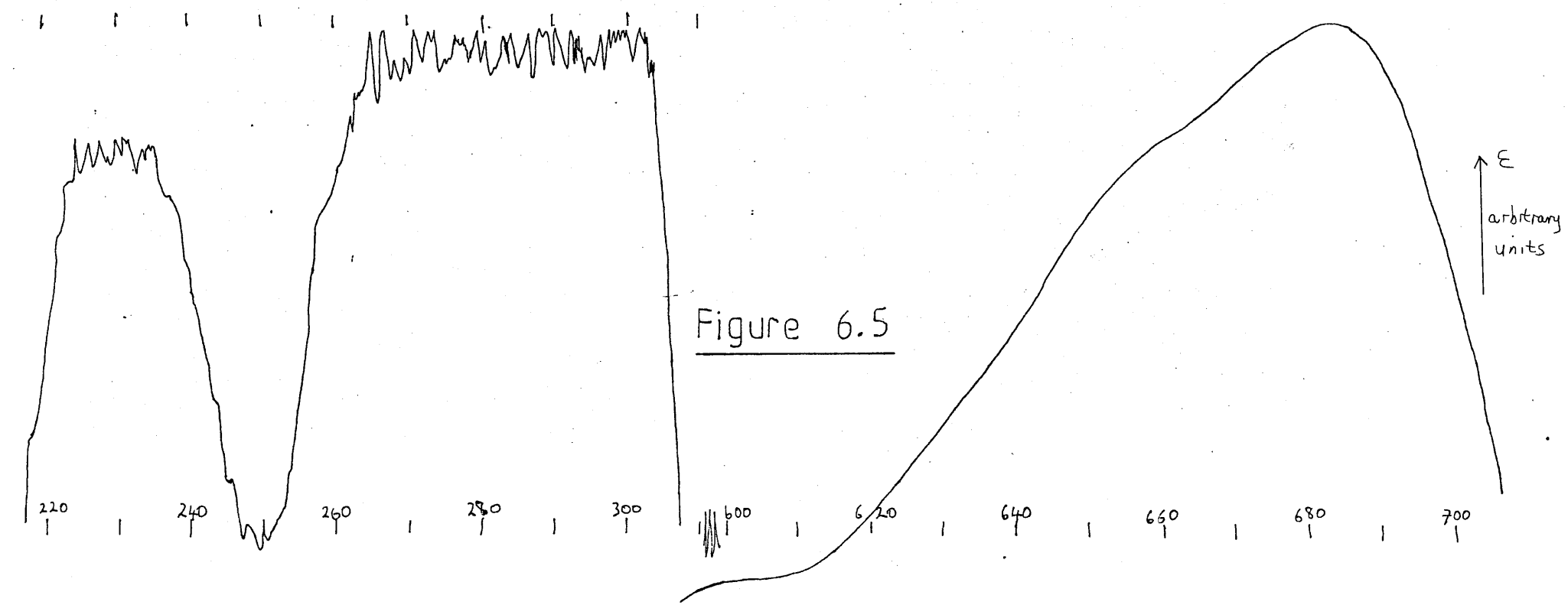

ε
arbitrary units
220
240
260
280
300
600
620
640
660
680
700

Figure 6.5

lost around 100°C to give the anhydrous compound.

Using anhydrous $CoBr_2$ and distilling on dried diethyl ether, hopefully to give $CoBr_2(Et_2O)_x$, gave rise to a blue solution and some green solid ($CoBr_2$), no doubt because diethyl ether is a poorer solvent and cannot dissolve $CoBr_2$ so readily.

The only other experiment using solely $CoBr_2$ in T.H.F. involved stirring such a solution under carbon monoxide to establish the lack of formation of any cobalt carbonyl compounds (in conjunction with experiments of chapter 2). In diethyl ether $CoBr_2$ and sodium wire also showed a lack of reactivity (by i.r. spectroscopy).

Experimental

For isolation of solid cobalt halide etherates, some anhydrous $CoBr_2$ was dried by heating in vacuo for two hours at 100°C in a round bottomed flask. Enough solvent to dissolve the solid was distilled on, in vacuo, then slow evaporation, usually under nitrogen, followed to form the solid. For the solution visible / U.V. and near i.r. spectra, the reaction vessel of Fig. 6.6 was attached to the vacuum line already containing roughly 0.04g $CoBr_2$ [1.83×10^{-4} moles] and the experiment proceeded from there.

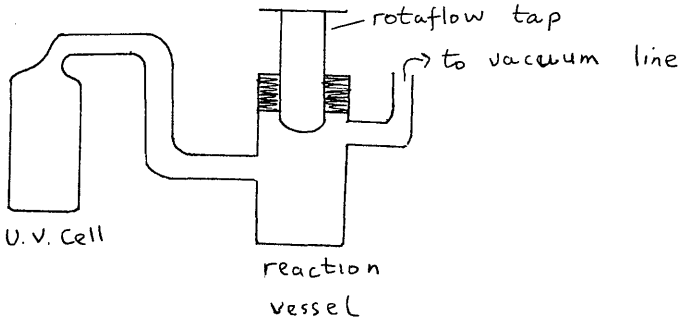


Figure 6.6

To make $CoBr_2(Et_2O)_x$ from $CoBr_2$, 0.653g cobalt metal [11.08×10^{-3} moles] was added to 25 ml of nitrogen saturated diethyl ether in a standard three necked, round bottomed flask. This was cooled in a dry ice / acetone slush bath ($-78^{\circ}C$) before 0.6 ml bromine [11.65×10^{-3} moles] - a slight excess of the halogen, as required - was slowly and carefully added through the septum cap. [Warning very exothermic reaction.] This was left for twelve hours in the slush bath, although a green solution was present after two hours, before being allowed to attain room temperature. In the T.H.F. analogue the same procedure was followed, using 0.647g cobalt metal [10.98×10^{-3} moles] and 0.7 ml bromine [13.59×10^{-3} moles] in 20 ml T.H.F. This initially gave a red solution which after half an hour became green.

Elemental analysis of solid $CoBr_2(T.H.F.)_x$ was :

found C15.22, H2.60, Br 48.3% ; calculated (for $CoBr_2(T.H.F.)_1$) C16.52, H2.78, Br 54.95%. Allowing for some air oxidation a compound of composition $CoBr_2(T.H.F.O_2)$ is postulated - this has calculated values C 14.9, H2.5 and Br 49.5 with a % error in C and Br of 2% and in H of 4%. There does not appear to be water present since the experimentally found C:H ratio is in agreement with the calculated ratio of these elements in T.H.F. only.

Discussion

As previously stated, $CoBr_2$ in T.H.F. contains tetrahedral Co^{2+}, whether coordination is by 4 T.H.F. or 4 Br^- (to give $[CoBr_4]^{2-}$) or a mixture of both is not known. If water is present coordination of Co^{2+} becomes six.

For the solid compound, Co^{2+} is coordinated by the four bromides, by comparison with literature spectra[313]. Previous work in the department using $CoCl_2$ in T.H.F. showed that the solid compound had composition

$CoCl_2(T.H.F.)_{1.5}$[225]. Evidence for such a compound has been given by no less a person than Chatt, who mentioned $CoCl_2(T.H.F.)_{1.5}$ as a blue solid which is thermally unstable but isolable[314]. The present work showed one T.H.F. molecule plus possibly oxygen to be present in the solid (although not directly bonded to Co^{2+}); presumably if the micro-analysis is accurate, air oxidation causes oxygen to replace or attack some of the T.H.F. in the lattice. Since $CoBr_2$ - etherates are adduct compounds T.H.F. is easily lost and the "bare" Co^{2+} then mops up any water present forming the hexahydrate species.

The solution spectra are harder to understand. Colour and the absorption of the compound (max $\sim$ 680 nm) indicate tetrahedral coordination, and the lack of activity of $CoBr_2$ as a catalyst in the disproportionation of $Co_2(CO)_8$ is strongly suggestive of the bromides being bound to Co^{2+} in solution.

The species made from the bare metal and halogen appeared to give a visible / U.V. spectrum consistent with a mixture of tetrahedral and octahedral coordination of Co^{2+} with absorptions in the 600 - 700 nm region due to tetrahedral structure and at 480 nm due to octahedral structure. A range of tetrahedral Co^{2+} complexes have had their solution visible / U.V. spectra recorded and this lends support to our assignment[315]. The spectrum of $[Co(H_2O)_6]^{2+}$ [7] has a similar line shape to the spectra being discussed here but at lower wavelength. Doubt still remains since bonding of Co^{2+} to the oxygen of T.H.F. will move the maximum absorption to lower wavelengths than bonding to halide, bringing the tetrahedral absorptions into the same region as octahedral absorptions. The solution of $CoBr_2(T.H.F.)_x$ absorbs at lower wavelengths than the solid complex suggesting some coordination by T.H.F. The two absorptions in the compound formed by metal plus halogen could be two different

octahedral complexes e.g. one with $2Br^-$ + 4T.H.F., the other with $4Br^-$ and 2T.H.F.

Comparison of these spectra with that of $Co(BF_4)_2$ in T.H.F. (Fig.2.44b) shows them to be very similar. It is suspected that there is $CoBr_2$ present in this compound as an impurity, giving rise to the spectrum. It is possible but we believe unlikely, that these complexes have similar spectra because Co^{2+} is tetrahedrally coordinated by 4 T.H.F. molecules. As stated earlier the halides are not thought to be uncoordinated to Co^{2+} because of the compound's lack of activity in disproportionation, and the visible / U.V. spectra of both compounds are too similar to be representative of different anions.

Time did not allow us to fully resolve this dilemma.

In conclusion it is very difficult to isolate solids of adducts of $CoBr_2$ without decomposition caused by removal of excess ligand and / or the presence of water.

3. TETRAPHENYLPHOSPHONIUM TETRACARBONYLCOBALTATE (-1)

Tetraphenylarsonium salts of $[Co(CO)_4]^-$ have been reported as isolable crystalline solids stable at 25°C[199]. By serendipity, the phosphorus analogue was made and isolated when the reaction of Ph_4PBr and $Co_2(CO)_8$ in diethyl ether was investigated (see chapter 2). The pale green solid was at first thought to be air stable over a period of time but later showed some decomposition noticeable by a darkening of hue until after a few months a black residue is left.

Usually the best method for preparing this compound was to react Ph_4PBr and $Co_2(CO)_8$ in T.H.F., until the i.r. spectrum showed $[Co(CO)_4]^-$ to be the only cobalt carbonyl containing species to be present. Removal of solvent under reduced pressure followed then deionised water was added to extract Co^{2+} from the residue. This mixture was filtered at the water pump and a green crystalline solid isolated. The i.r.

spectrum of the solid (at two concentrations) is shown in Fig. 6.7 - the second spectrum is to show the signals due to the phenyl rings. The i.r. spectrum of Ph_4PBr is shown in Fig. 6.8 for comparison. The signals can be assigned as shown in Table 6.1

Table 6.1

i.r. Assignments of $Ph_4PCo(CO)_4$ (solid).

$\bar{\nu}$ cm^{-1}	Assignment
3060	Aryl C - H
3040, 3000	Aryl C - H
2005	$[Co(CO)_4]^-$ - A_1 mode
1875	$[Co(CO)_4]^-$
1587, 1575, 1485	Aromatic C - C
1437	Ph - P Band I
1400	C - O ?
1340, 1315, 1190, 1167	$[Ph_4P]^+$ (c.f. Ph_4PBr spectrum)
1110	Ph - P Band II
1030	$[Ph_4P]^+$
1000	Ph - P Band III
757	$[Ph_4P]^+$ (c.f. Ph_4PBr spectrum, signals at 767 & 755)
725	Ph - P Band IV
690	C - H aromatic
620	$[Ph_4P]^+$
555	$[Co(CO)_4]^-$ (lit. values: 553s & 528w)
537	Ph - P Band V
470, broad	$[Ph_4P]^+$ (seen as 2 weak signals in Ph_4PBr)

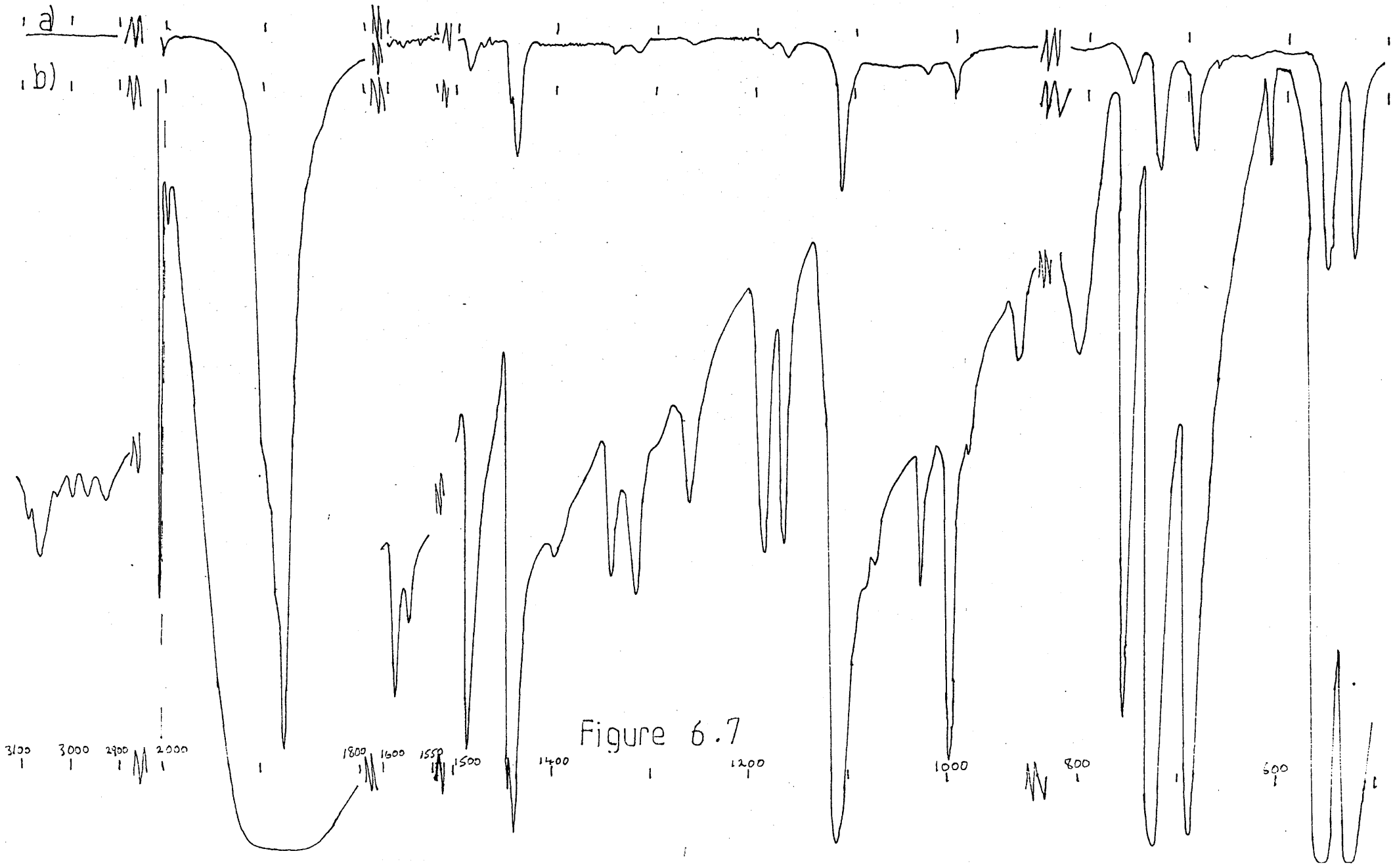

a)
b)
3100
3000
2900
2000
1800
1600
1550
1500
1400
1200
1000
800
600

Figure 6.7

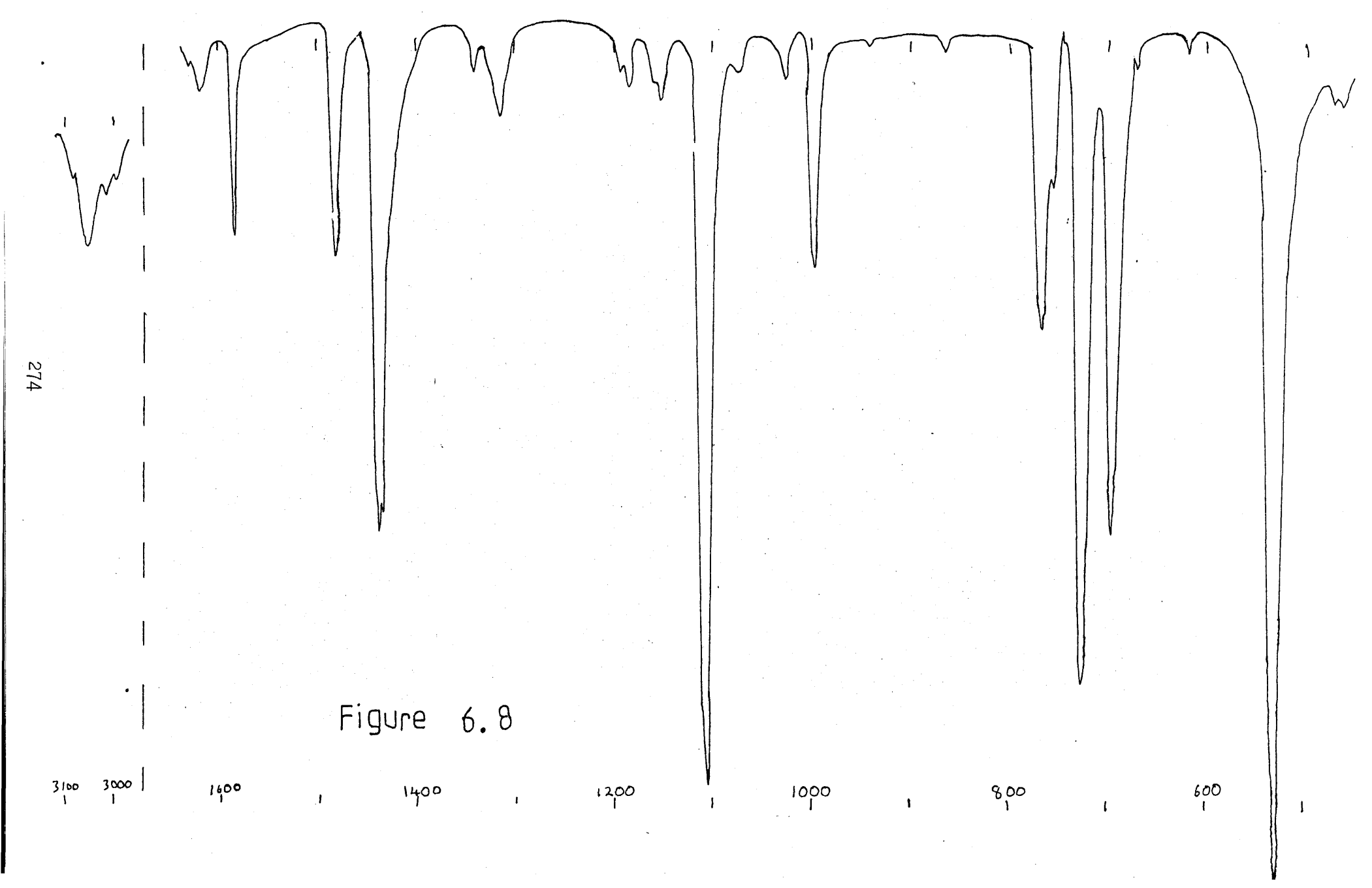


Figure 6.8

The solid Raman spectrum was also recorded, using the KBr disc of the i.r. experiment, and is shown in Fig. 6.9.

An effort to get the solution Raman spectrum of the compound failed because no matter what care was taken in preparing the sample, with T.H.F. as the solvent, it decomposed before the spectrum had been run. Elaborate methods included preparing the sample in vacuo and sealing off the Raman cell in vacuo.

The visible / U.V. spectrum of the solid showed a broad featureless absorption between 350 - 500 nm alongside bands due to vibrations of the phenyl rings at lower wavelengths than 300 nm. Further characterisation was attempted using n.m.r. techniques. The ^{1}H decoupled ^{31}P n.m.r. of $Ph_4PCo(CO)_4$ in $CDCl_3$ showed a singlet at 23.2 p.p.m. which agrees reasonably with literature values of similar compounds e.g. Ph_4PBr has a ^{31}P n.m.r. chemical shift of 20.8 p.p.m. The ^{1}H n.m.r. of the cobalt compound was more difficult to obtain because of problems of dissolving the species in $CDCl_3$ without forming any solid. Eventually this hurdle was overcome and the spectrum illustrated in Fig. 6.10a was obtained. The ^{1}H n.m.r. spectrum of Ph_4PBr is shown for comparison (Fig. 6.10b).

Some of the white decomposition product, from the reaction of $Ph_4PCo(CO)_4$ and $CDCl_3$, was isolated and its i.r. spectrum, with assignments where possible, is shown in Fig. 6.11.

The melting point range of $Ph_4PCo(CO)_4$ was determined to be 107 - 109°C, with decomposition to a black tar. To establish what this could be, decomposition of the compound, under various circumstances, was attempted. Firstly, the compound was heated in the air, using a Bunsen. It gave off white fumes and the green solid turned black, via a green / brown intermediate. A more controlled experiment of heating the compound

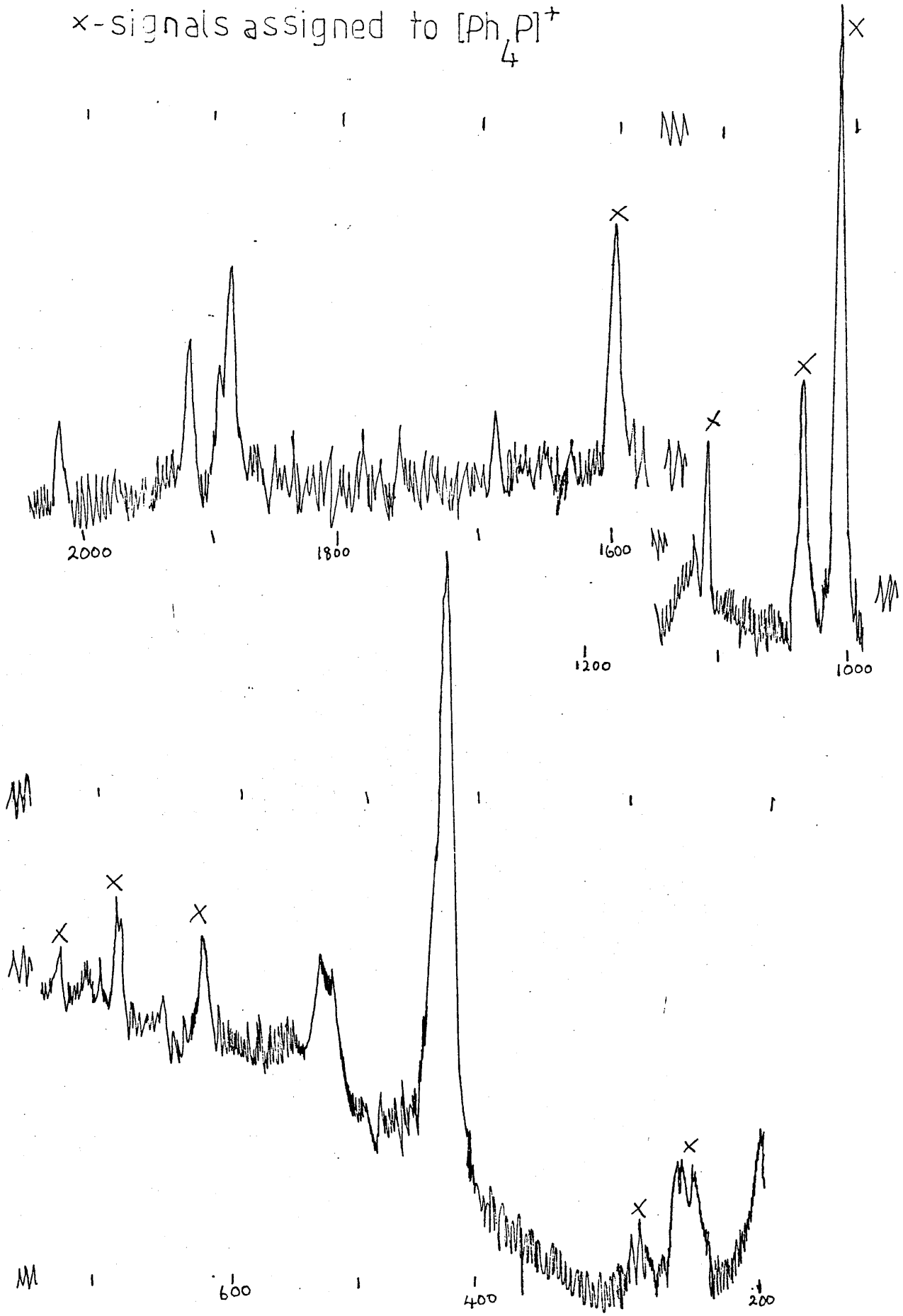

x-signals assigned to $[Ph_4P]^+$
2000
1800
1600
1200
1000
600
400
200

Figure 6.9

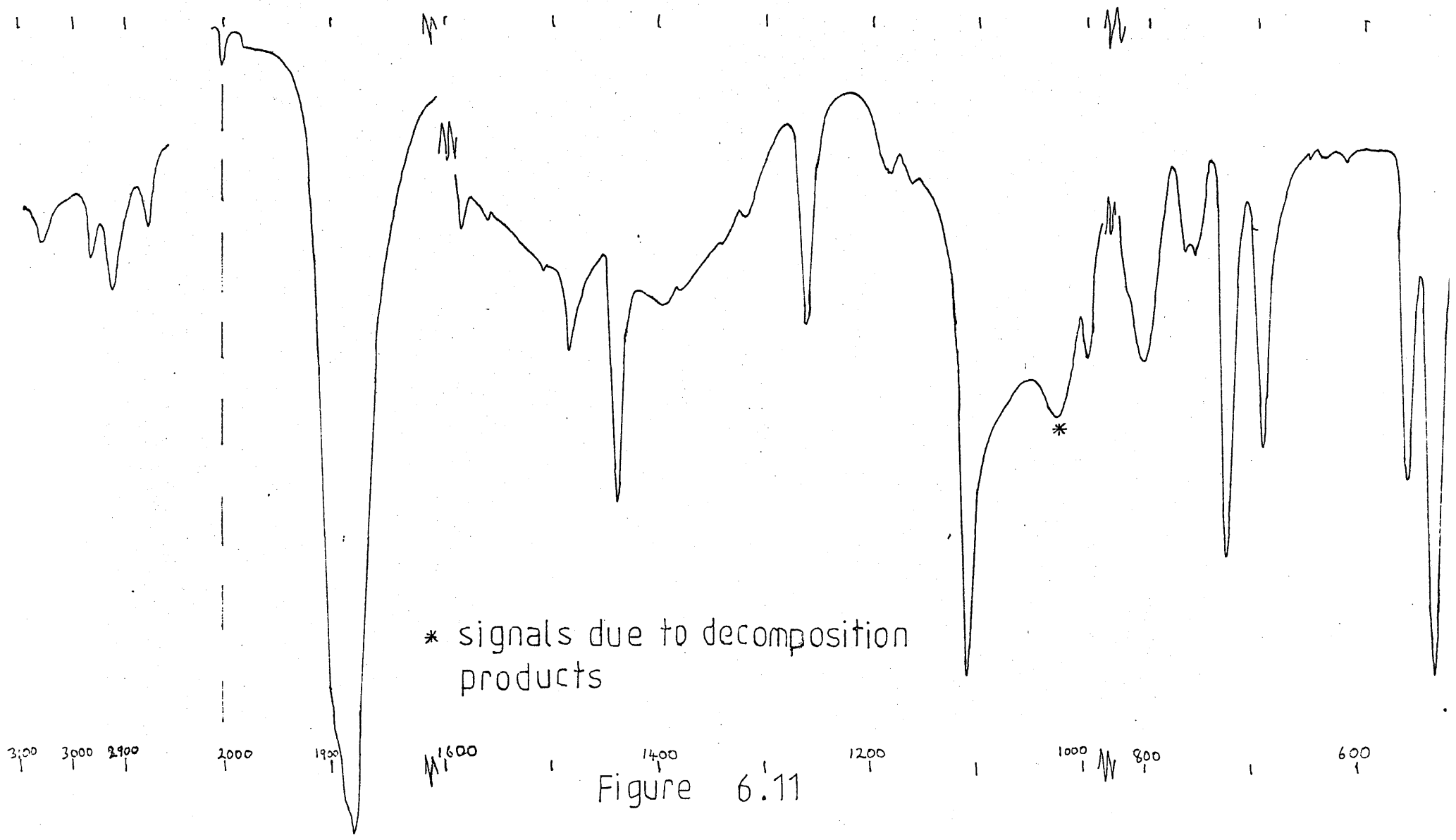

3100
3000
2900
2000
1900
1600
1400
1200
1000
800
600
* signals due to decomposition products

Figure 6.11

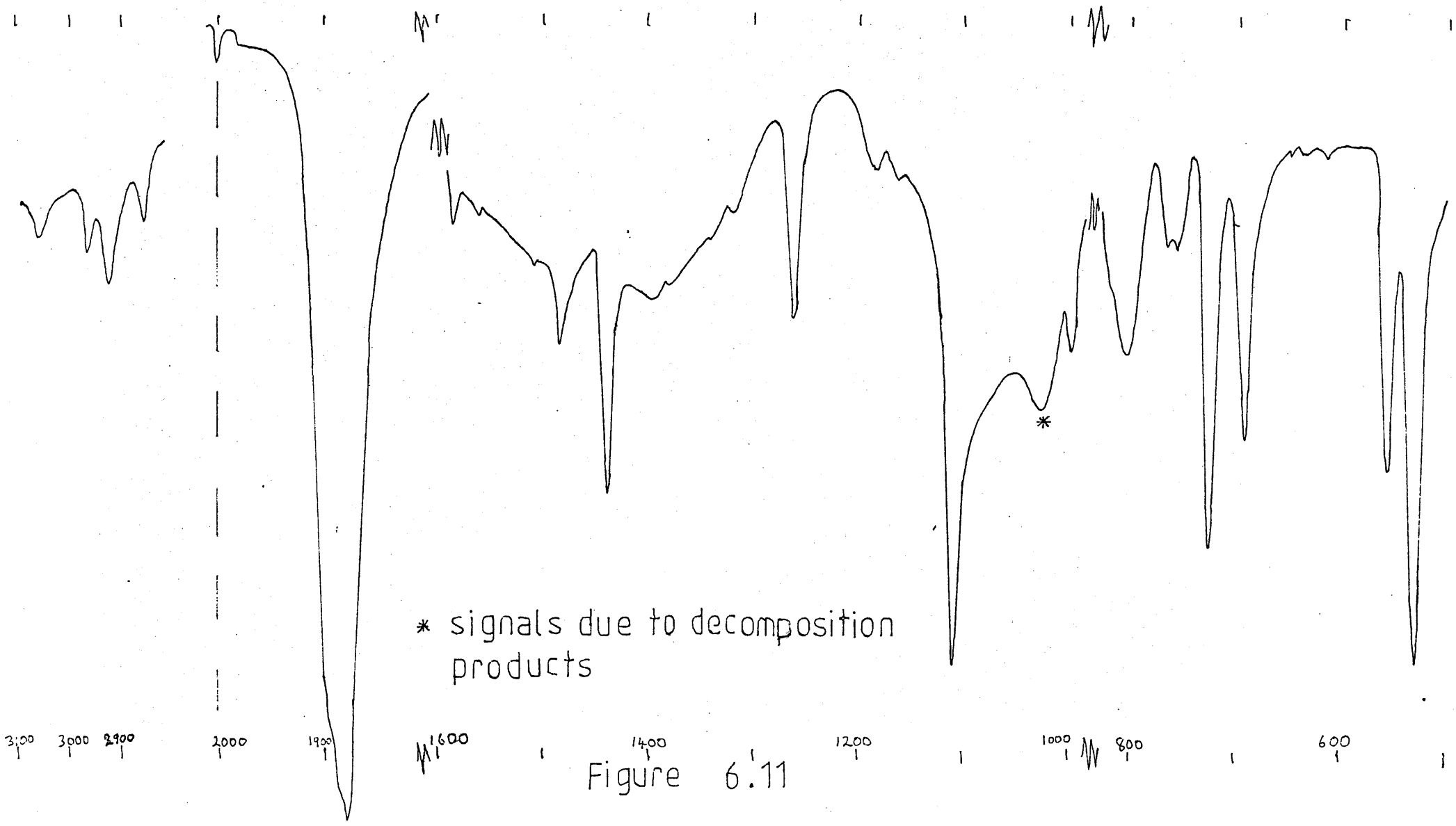

3100
3000
2900
2000
1900
1600
1400
1200
1000
800
600
* signals due to decomposition products

Figure 6.11

to 110°C in the air, using a heating tape, gave similar results. The i.r. spectra of the resulting products for both these experiments are shown in Fig. 6.12.

Presumably these show some derivative of the phenyl part of the compound.

Next the compound was heated at 120°C, in vacuo. Whether this is done for two hours or two weeks, the result is the same. There is charring of the sample on the surface and the i.r. spectrum (see Fig. 6.13) shows a strong absorption for the carbonyl with very little overall change from the compound in its natural state.

Finally air oxidation of $Ph_4PCo(CO)_4$ was achieved. Over one month there is a marked darkening of the colour of the sample but its i.r. spectrum is identical to that of the virgin compound. Over a year however the i.r. spectrum of Fig. 6.14 is obtained, with no carbonyl stretches in evidence.

By comparison with Ph_4PBr (Fig. 6.8), the strong signals can be assigned to $[Ph_4P]^+$ - perhaps the hydroxide or carbonate has been formed.

The reactions of $Ph_4PCo(CO)_4$ were as expected. Unfortunately the compound is insoluble in water, diethyl ether and toluene although it is soluble in T.H.F. There appears to be some reaction when EtOH and $CHCl_3$ are used as solvents and so investigation of the reactions of the compound were limited. As shown earlier, in chapter 2, it does not react with Co^{2+} (as the Br^- or $[BF_4]^-$ salts). With MeI and α,α' - dibromo - o - xylene reaction occurs to give the expected products $MeCo(CO)_4$ and 2-indanone. With $Co_4(CO)_{12}$, under carbon monoxide, $Co_2(CO)_8$ and $[Co(CO)_4]^-$ were formed while under nitrogen the carbonyl deficient cluster species $[Co_3(CO)_{10}]^-$ was found in addition to the reactants.

It was also established that $Ph_4PCo(CO)_4$ will remain stable in vacuo,

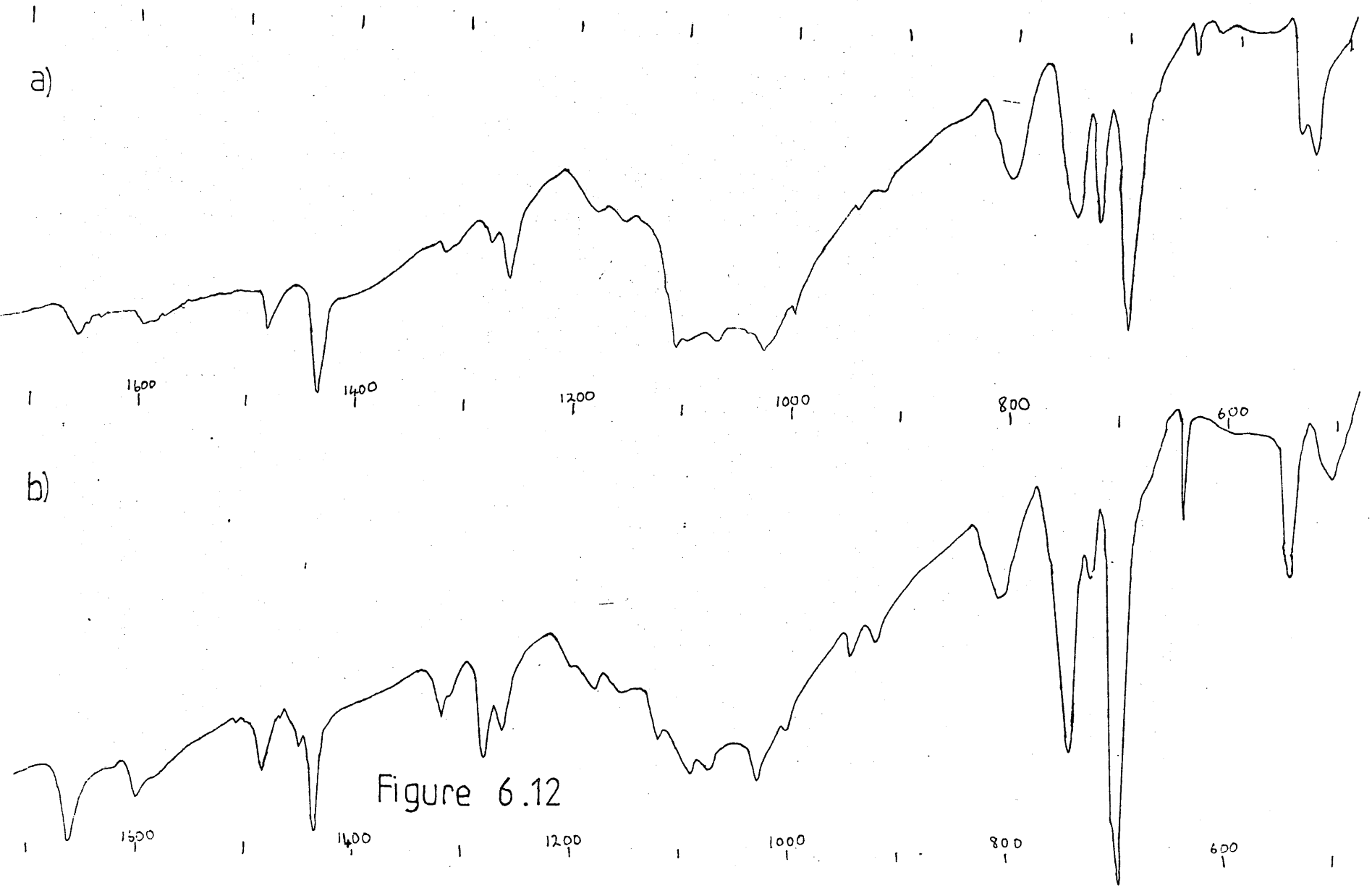


Figure 6.12

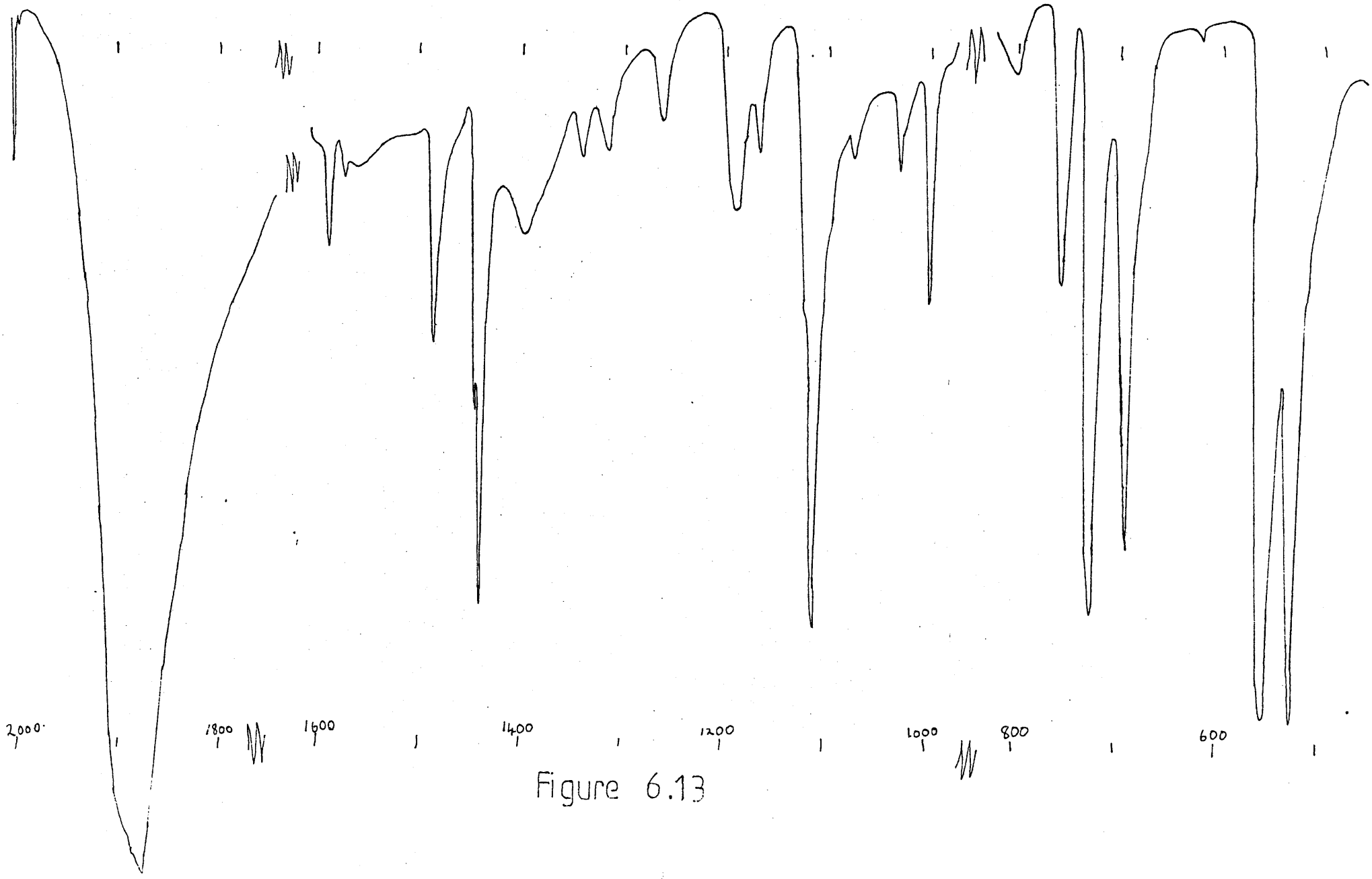


Figure 6.13

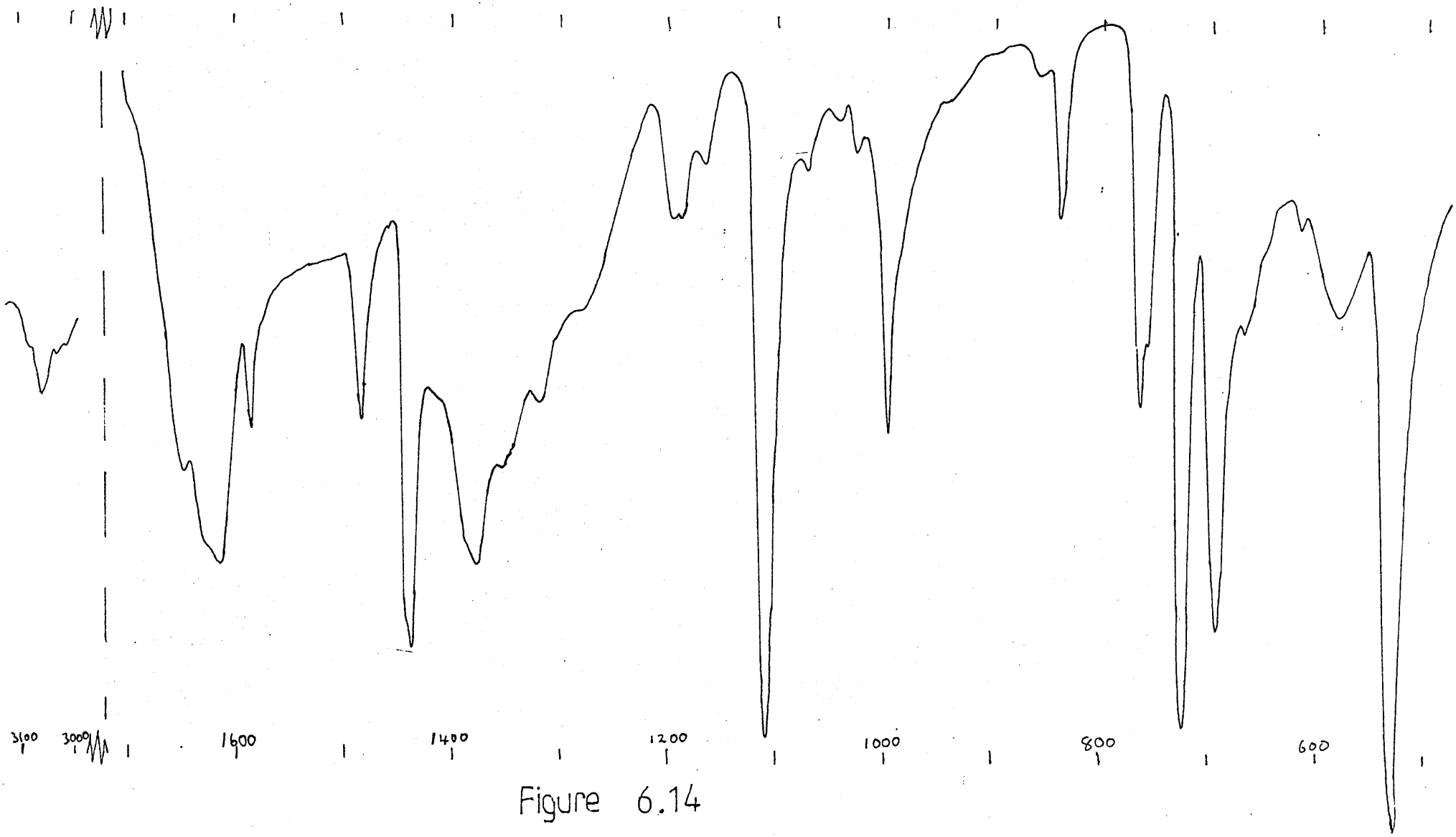


Figure 6.14

with or without the presence of light, for upwards of a year whereas in air decomposition will take place.

Experimental.

A typical preparation of $Ph_4PCo(CO)_4$ is outlined beneath. 1.032g $Co_2(CO)_8$ [3.02×10^{-3} moles] and 1.413g Ph_4PBr [3.37×10^{-3} moles] were placed, under carbon monoxide, in a standard reaction vessel fitted with a stirrer bar, along with 60 ml T.H.F. Stirring for one hour gave a green solution which was filtered through siliconised, dry, glass wool and the solvent removed under reduced pressure. Under nitrogen, the residue was mixed, by stirring, with 3 x 10 ml lots of warm, deionised water (to remove Co^{2+} and unreacted Ph_4PBr) and filtered to give a pale green solid and a pink aqueous solution of Co^{2+}. The solid was then dried overnight, in vacuo, before use. The elemental analysis of the compound was:

Calculated:	C 65.89	H 3.96	P 6.07
Found 1 :	64.8	3.5	5.78
2 :	63.73	3.97	5.76

P was found by gravimetric technique since the presence of a heavy metal, cobalt, made the normal method of determination impractical. For n.m.r. samples, the n.m.r. tube was fitted with a septum cap, and a syringe needle, attached to the vacuum line by means of a length of tubing, was inserted through the cap. In this way the air could be pumped out of the tube and replaced by nitrogen. A fresh, filtered, sample of $Ph_4PCo(CO)_4$ in $CDCl_3$ was syringed into the n.m.r. tube, and the cap sealed with parafilm, then the n.m.r. spectrum was recorded. The ^1H n.m.r. was recorded on the Perkin Elmer 90MHz and the ^{31}P n.m.r. was recorded on Varian XL - 100.

The decomposition experimental apparatus consisted of an evacuated long test tube, containing the sample spread along its length, being

attached, using a stopcock tap, to the vacuum line. Heating tape was wound around the test tube and allowed to reach the required temperature. Periodically the tube was opened to the vacuum line to allow any carbon monoxide to be pumped off.

Discussion.

Although elemental analysis was not very accurate (the errors in C, H and P were respectively $\pm$ 3.3%, $\pm$ 0.3%, $\pm$ 5.1%) the spectroscopic techniques confirm the molecular formula assigned to this compound, with $[Co(CO)_4]^-$ most likely to be tetrahedral and the cation closely related in structure to that of the simple halide salts. $Ph_4PCo(CO)_4$ is a useful method of storing $[Co(CO)_4]^-$ in the solid form, and has the advantage over $[Fe(\underline{o}phen)_3][Co(CO)_4]_2$ since weight for weight it has a higher percentage of $[Co(CO)_4]^-$ in it. Further attention to this compound will no doubt pay handsome dividends.

CHAPTER 7

PERSPECTIVE

CHAPTER 7 - PERSPECTIVE

Metal carbonyl chemistry has come a long way since the first experiments of W. Hieber. In 1940 metal carbonyls occupied a unique place among complex compounds because their composition was not governed by considerations of the usual coordination number of the metals concerned but primarily because of their tendency to form closed electronic shells[40]. Since then, as pointed out in chapter 1, they have lost this uniqueness. These compounds were discussed in Emeleus and Anderson's classical book which was also responsible for some educated forecasts. The constitution of metal carbonyls was the stumbling block of the valence theories of the day, with their non polar character and diamagnetism of the simple compounds in contrast with the properties of other transition metal compounds. The formal valency was not recognised but there was evidence of a simplistic relationship between the atomic number of the metal and composition of the simple metal carbonyls. The authors regarded the CO group in carbonyls as a little modified carbon monoxide molecule coordinated to a central metal atom, as other neutral molecules or ions are linked in complex salts to central cations - this view of bonding had been foreseen by Mond in 1892. The ideas of π type dative bonds (in back bonding) and of bridging carbonyl groups between metal atoms of polynuclear carbonyls were also presented, with the structure of $Fe_2(CO)_9$ lending experimental support to the latter suggestion. It was felt that the concept of electron deficient bonds, as in polymeric metal alkyls, could be invoked, by considering one orbital of the carbonyl group (containing a lone pair of electrons) overlapping symmetrically a vacant orbital of each metal atom.

Many ideas expressed in the preceeding paragraph have of course been vindicated, some of them undergoing a degree of modification. It can take many years, and the advent of new skills and technology, to solve such problems. More recently a review of mechanisms of carbon monoxide replacement in metal carbonyls has shown the usefulness of kinetic studies in determining the lability of different types of carbonyls in a compound and that it is not always a simple case of extrapolating ideas in one field to compounds of a different type, e.g. square planar Pt(II) complexes undergo associative S_N2 substitution reactions but four coordinate $Ni(CO)_4$ reacts by a dissociative mechanism[316].

The most recent, startling idea regarding carbon monoxide as a ligand is that it may be a six electron ligand[317]. The compound tetracarbonyl - -(η^5cyclopentadienyl) niobium, $cpNb(CO)_4$, can react to give $cp_3Nb_3(CO)_7$ by photolysis in hexane at 18°C. X Ray diffraction techniques have shown one of the seven carbon monoxide ligands acting as a $\eta^2(\mu_3\text{-}C,\mu_2\text{-}O)$ bridge symmetrically facing a nearly equilateral niobum triangle, with a resultant lengthening of the C - O bond to 1.303 Å, and shift of the $\bar{\nu}$(CO) absorption to 1330 cm^{-1}. The carbonyl ligand is thought to be acting as a six electron ligand towards three metal centres.

And so to this work, which is in no manner complete. Several points need to be clarified, but time ran out.

It would be interesting to conduct the experiments of chapter 3 in a nitrogen atmosphere to see if further intermediate "carbonyl deficient" clusters could be recognised. The kinetic work on the disproportionation of $Co_2(CO)_8$ in T.H.F., with or without catalytic species, at 0°C, would be benificial in elucidating the reaction mechanism(s) of this and similar types of reactions. Naturally the same work in toluene would show, when taken in conjunction with earlier work in this

department[225], any differences in reaction pathways caused by the lowering of temperature. Also in this vein, monitoring the rate of evolution of carbon monoxide from such reactions would supply information - this was not attempted in the present work.

It would be amusing to establish what type of reactions $Co_4(CO)_{12}$ would undergo under the type of conditions used throughout for $Co_2(CO)_8$. The experiment involving the setting up of a reductive couple, using sodium and copper, in a diethyl ether solution of $Co_2(CO)_8$ must be repeated, to find out exactly what is produced in the reduction of $Co_2(CO)_8$, and by comparison with the results of chapters 3 and 4 test the suspicions that $Co_2(CO)_8$ and sodium amalgam in diethyl ether react mainly by disproportionation, not reduction.

There are many loose ends to tie up, e.g. the unexplained i.r. spectra; the species denoted as "carbon monoxide deficient" clusters of cobalt; the mysteries of the sodium amalgam or mercury / LiBr reactions with $Co_2(CO)_8$ described in chapter 4, including the variation in the ratio of complexes found in solution.

No doubt these will be explained some day and fit in neatly with that present day scheme of thinking. Until then, we must wait.

REFERENCES

1. The Shorter Oxford English Dictionary, 3rd. Edn., C.T. Onions Ed., Clarendon Press, (1956 - revised).
2. The Encyclopaedia of the Chemical Elements, C.A. Hampel Ed., Reinhold, (1968), pp154.
3. A Short History of Chemistry, 3rd. Edn., J.R. Partington, MacMillan, (1957), p10.
4. The Merck Index, 9th. Edn., Merck, (1976), no 2379.
5. The Chemical Elements and Their Compounds Vol. II, N.V. Sidgewick, Clarendon Press, (1950), 1314 - 1454.
6. Complexes and First Row Transition Elements, D. Nicholls, MacMillan, (1974).
7. Advanced Inorganic Chemistry, 3rd. Edn., F.A. Cotton and G. Wilkinson, J. Wiley & Sons, (1972).
8. R.F. Heck, J. Amer. Chem. Soc. 85, (1963), 657.
9. J.A. McCleverty, A. Davison, and G. Wilkinson, J. Chem. Soc. (1965), 3890.
10. The Chemistry of Cyano Complexes of Transition Metals, A.G. Sharpe, Acad. Press, (1976), 159.
11. E. Krause and A. Van Grosse, Die Chemie der Metall - Orgnischen Verbindugen, Borntraeger Berlin, (1937) - cited in ref. 14.
12. L.C. Cadet de Gassicourt, Mem. Math. Phys. 3, (1760), 623 - cited in ref. 14.
13. J.S. Thayer, J. Chem. Ed. 46, (1969), 764.
14. J.S. Thayer, Adv. Organomet. Chem. 13, (1975), 1.
15. E. Frankland, Phil. Trans. 142, (1852), 417 - cited in ref. 14.
16. D. Mendeleyeef, Annalen. Suppl. 8, (1871), 133-229.
17. M.P. Schutzenberger, Annales 15, (1868), 100.

18. L. Mond, C. Langer, and F. Quincke, J. Chem. Soc. 57, (1890), 749.

19. L. Mond and F. Quincke, J. Chem. Soc. 59, (1891), 604.

20. P.E.M. Berthelot, Compte Rend. 112, (1891), 1343.

21. J. Dewer and H.O. Jones, Proc. Roy. Soc. (London) A76, (1905), 558.

22. Ibid. A79, (1906), 66.

23. Late L. Mond, H. Hirtz, and M.D. Cawap, J. Chem. Soc. 97, (1910), 798.

24. A. Job and A. Cassals, Compte. Rend. 183, (1926), 58, 392.

25. A. Job and J. Rouvillois, ibid. 187, (1928), 564.

26. W. Manchot and W.J. Manchot, Z. Anorg. Allgem. Chem. 226, (1936), 385.

27. E.R. Corey, L.F. Dahl and W. Beck, J. Amer. Chem. Soc. 85 (1963), 1202.

28. W. Hieber and H. Lagally, Z. Anorg. Allgem. Chem. 245, (1940), 321.

29. W. Hieber and H. Fuchs, ibid. 248, (1941), 256.

30. W. Hieber and H. Lagally, ibid. 251, (1943), 96.

31. W. Hieber and H. Stallman, Z. Elektrochem. 49, (1943), 228.

32. E.O. Brimm, M.A. Lynch Jnr., and W.J. Sesay, J. Amer. Chem. Soc. 76, (1954), 3831.

33. G.R. Natta, F. Ercoli, F. Calderazzo, A. Alberolo, P. Coradini and G. Allegra, Atti Accad. Naz. Lincei. Rend. Classe Sci. Fis. Mat. Nat. 27, (1959), 107 - cited in ref. 37.

34. J.C. Hileman, D.K. Huggins, and H.D. Kaesz, J. Amer. Chem. Soc. 83, (1961), 2953.

35. K.K. Joshi and P.L. Pauson, J. Chem. Soc. (1962), 336.

36. A.N. Nesmeyanov, K.N. Anisimov, N.E. Kolobova, and I.S. Kolomnikov, Izv. Akad. Nauk S.S.S.R. Otd. Khim. Nauk, (1963), 193.

37. J.C. Hileman, Prep. Inorg. Reactions Vol. I, W.L. Jolly Ed., John Wiley & Sons, Ch.4, (1964), 77 - 120.

38. R.L. Mond and A.E. Walles, J. Chem. Soc. 121, (1922), 29.

39. The Electronic Theory of Valency, N.V. Sidgewick, Oxford Uni. Press, (1927).

40. Modern Aspects of Inorganic Chemistry, H.J. Emeleus and J.S. Anderson, Routeledge and Kegan Paul Ltd., (1938).

41. I. Langmuir, Science 54, (1921), 59.

42a L.O. Brockway and J.S. Anderson, Trans. Faraday Soc. 33, (1937), 1233.

42b L.O. Brockway and P.C. Cross, J. Chem. Phy. 3, (1935), 828.

42c L.O. Brockway, R.V.G. Ewens, and M.W. Listen, Trans. Faraday Soc. 34, (1938), 1350.

43. R.V.G. Ewens and M.V. Listen, Trans. Faraday Soc. 35, (1939), 681.

44. J.S. Anderson, Quart. Rev. 1, (1948), 331.

45. W. Rüdorff and U. Hofmann, Z. Physikal Chem. 28, (1935), B351.

46. R. Brill, Z. Krist. 65, (1927), 85.

47. H.M. Powell and R.V.G. Ewens, J. Chem. Soc. (1939), 286.

48. K.A. Jensen, Z. Anorg. Chem. 252, (1944), 234.

49. R.V.G. Ewens, Nature 161, (1948), 530.

50. L.F. Dahl, E. Ishishi, and R.E. Rundle, J. Chem. Phy. 26, (1957), 1750.

51. R.L. Pruett and J.E. Wyman, Chem. & Ind. (1960), 119.

52. F. Calderazzo, R. Cini, P. Corradini, E. Ercoli, and G. Natta, Chem. & Ind. (1960), 500.

53. P.L. Pauson, Proc. Chem. Soc. (1960), 297.

54. Isolated Bond Strength vs Molecular Stability for the Metal Carbonyls, H.E. Podall, Melpar Inc., Falls Church Virginia, (1962), pp 1-10.

55. R.S. Nyholm. Proc. Chem. Soc. (1961), 273.

56. E.W. Abel, Quart. Rev. 17, (1963), 133.

57. Valence, 2nd. Edn., C.A. Coulson, Oxford Uni. Press, (1961), 222.

58. J. Chatt, P.L. Pauson, and L.M. Venanzi, Organometallic Chemistry, H. Zeiss Ed., Reinhold, (1965), Ch 10, P468.

59. W. Hieber, R. Nast, and J. Sedlmeier, Angew. Chem. 64, (1952), 465.

60. W. Hieber and H. Schulten, Z. Anorg. Allgem. Chem. 232, (1937), 17.

61a W. Hieber and F. Leutert, Chem. Ber. 64, (1931), 2832.

61b W. Hieber, Z. Elektrochem. 40, (1934), 158.

62. W. Hieber and F. Sonnerkalb, Chem. Ber. 61, (1928), 558.

63. W. Hieber, Angew. Chem. 55, (1942), 7.

64. H.W. Sternberg, I. Wender, R.A. Friedel, and M. Orchin, J. Amer. Chem. Soc. 75, (1953), 2717.

65. K. Noack and F. Calderazzo, J. Organomet. Chem. 10, (1967), 101.

66. P.S. Braterman and R.J. Cross, Chem. Soc. Rev. 2, (1973), 271.

67. W. Reppe and H. Vetter, Ann. 582, (1953), 1, 38, 72, 87, 133.

68. H.E. Podall, J. Chem. Ed. 38, (1961), 187.

69a A. Wojcicki and F. Basolo, J. Amer. Chem. Soc. 83, (1961), 525.

70. F.A. Cotton, A.K. Fischer, and G. Wilkinson, J. Amer. Chem. Soc. 81, (1959), 800.

71. The Fisher - Tropsch and Related Synthesis, H.H. Storch, N. Golumbic, and R.B. Anderson, John Wiley & Son Inc., New York N.Y. (1951).

72. Acetylenic and Carbon Monoxide Chemistry, J. Copenhaver and M.H. Boelow, (1949).

73. T.J. Keely and P.L. Pauson, Nature 168, (1951), 1039.

74. S.A. Miller. J.A. Tebboth, and J.F. Tremaine, J. Chem. Soc. (1952), 632.

75. G. Wilkinson, C.M. Rosenblum, M.C. Whiting, and R.B. Woodward, J. Amer. Chem. Soc. 74, (1952), 2125.

76. C.W. Bird, Chem. Rev. (1962), 283.

77. J. Chatt and B.L. Shaw, J. Chem. Soc. (1959), 705; (1960), 1718.

78a G. Yagupsky, W. Mowat, A. Shortland and G. Wilkinson, J.C.S. Chem. Comm. (1970), 1369.

78b F. Hue, W. Mowat, A. Shortland, A.C. Skapski, and G. Wilkinson, ibid. (1971), 1079.

79. P.S. Braterman and R.J. Cross, J.C.S. Dalton (1972), 657.

80. P.G. Lenhert and H.D. Crowfoot, Nature 192, (1961), 937.

81. W. Hieber, Adv. Organomet. Chem. 8, (1970), 1.

82a W. Hieber, W. Beck, and G. Braun, Angew. Chem. 72, (1960), 795.

82b W. Hieber, H. Schulten, and R. Marin, Z. Anorg. Chem. 240, (1939), 261.

83. H.W. Sternberg, I. Wender, R.A. Friedel, and M. Orchin, J. Amer. Chem. Soc. 75, (1953), 3148.

84. Reaction of Transition Metal Complexes, J.P. Candlin, K.A. Taylor, and D.T. Thompson, Elsevier, (1968).

85. R.A. Friedel, I. Wender, S.L. Shuffler, and H.W. Sternberg, J. Amer. Chem. Soc. 77, (1955), 3951.

86. O.S. Mills and G. Robinson, Proc. Chem. Soc. (1959), 156.

87. F. Basolo and A. Wojcicki, J. Amer. Chem. Soc. 83, (1961), 520.

88. G.G. Sumner and H.P. Klug, Am. Cryst. Ass. Annual Meeting, Boulder, Colorado, (1961), Abstract No. G7.

89. G. Bor, Spectrochim. Acta 19, (1963), 1209.

90. K. Noack, Spectrochim. Acta 19, (1963), 1925.

91. O.S. Mills (quoted by R.S. Nyholm), Proc. Chem. Soc. (1961), 287.

92. G. Bor, Spectrochim. Acta 19, (1963), 2065.

93. G. Bor and K. Noack, J. Organomet. Chem. 64, (1974), 367.

94. S. Onako and D.F. Shriver, Inorg. Chem. 15, (1976), 915.

95. H.B. Gray, M.S. Wrighton et al. Inorg. Chem. 16, (1977), 1554.

96a R. Whyman, Nature (London) Phys. Sci. 230, (1971), 139.

96b E.E. Ernstbrunner and M. Kilner, J.C.S. Dalton (1976), 417.

96c G. Bor, U.K. Dietler and K. Noack, J.C.S. Chem. Comm. (1976), 914.

97. R.L. Sweany and T.L. Brown, Inorg. Chem. 16, (1977), 415.

98. D.L. Lichtenberger and T.L. Brown, Inorg. Chem. 17, (1978), 1381.

99a P. Corradini, J. Chem. Phy. 31, (1959), 1676.

99b D.L. Smith, J. Chem. Phy. 42, (1965), 1460.

100. F.A. Cotton, Inorg. Chem. 5, (1966), 1083.

101. B.F.G. Johnson and R.E. Benfield, J.C.S. Dalton (1978), 1554.

102. R.F. Heck, Adv. Organomet. Chem. 4 (1966), 243.

103. W. Hieber, G. Braun, and W. Beck, Chem. Ber. 93, (1960), 901.

104. R.F. Heck and D.S. Breslow, J. Amer. Chem. Soc. 83, (1961), 4023.

105. R.F. Heck, J. Amer. Chem. Soc. 85, (1963), 1460.

106. R.F. Heck and D.S. Breslow, J. Amer. Chem. Soc. 84, (1962), 2499.

107. R.F. Heck and D.S. Breslow, J. Amer. Chem. Soc. 85, (1963), 2779.

108. R.F. Heck and D.S. Breslow, Actes 2e Congr. Intern. Catalyse, Paris Techip, Paris, (1961), 171.

109. L. Markó, G. Bor, G. Almasy, and P. Szabo, Brennstoff Chem. 44, (1963), 184.

110. R.F. Heck, J. Amer. Chem. Soc. 87, (1965), 4727.

111. H. des Abbayes and A.B. Buloup, J. Organomet. Chem. 179, (1979), C21.

112. V. Galamb, G. Pályi, F. Cser, M.G. Furmanova, and Yu. T. Struchkov, J. Organomet. Chem. 209, (1981), 183.

113. H. Alper and H. Des Abbayes, J. Organomet. Chem. 134, (1977), C11.

114. R.F. Heck, Adv. Catalysis 26, (1977), 323,

115. H. Alper, J. Organomet. Chem. Library 1, (1976), 305.

116a A.J. Chalk and J.F. Harrod, Adv. Organomet. Chem. 6,(1968), 119.

116b Organic Synthesis via Metal Carbonyls Vol. I, P. Pino and I. Wender Eds., Wiley, (1968).

117. L. Kirch and M. Orchin, J. Organomet. Chem. 162, (1978), 189.

118. P. Wermer, B.S. Ault, and M. Orchin, J. Organomet. Chem. 162, (1978), 189.

119. P. Pino, J. Organomet. Chem. 200, (1980), 223.

120. J.A. Rochand M. Orchin, J. Organomet. Chem. 172, (1979), C27.

121. J. Halpern, Adv. Catalysis 11, (1959), 324.

122. M. Orchin, Adv. Catalysis 16, (1966), 1.

123. A. Sacco and M. Freni, J. Inorg. Nucl. Chem. 8, (1958), 566.

124. M. Absi-Halabi, J.D. Atwood, N.P. Forbus, and T.L. Brown, J. Amer. Chem. Soc. 102, (1980), 6248.

125. N.E. Schore, C.S. Ilenda, and R.G. Bergman, J. Amer. Chem. Soc. 99, (1977), 1781.

126. R.L. Sweany, Inorg. Chem. 19, (1980), 3512.

127. F. Ungváry and L. Markó, J. Organomet. Chem. 193, (1980), 383.

128. R.N. Wegman and T.L. Brown, J. Amer. Chem. Soc. 102, (1980), 2494

129. N.P. Forbus, R. Oteiza, S.G. Smith, and T.L. Brown, J. Organomet. Chem. 193, (1980), C71.

130. R.L. Sweany and T.L. Brown, Inorg. Chem. 16, (1971), 421.

131a V. Bellagamba, R. Ercoli, A. Gamba, and G.B. Suffritti, J. Organomet. Chem. 190, (1980), 381.

131b V. Bellagamba and A. Gamba, J. Organomet. Chem. 212, (1981), 125.

132a F. Ungváry, J. Organomet. Chem. 36, (1972), 363.

132b F. Ungváry and L. Markó, Inorg. Chim. Acta 4, (1970), 324.

132c F. Ungváry and L. Markó, J. Organomet. Chem. 71, (1974), 283.

133. J.K. Ruff, Inorg. Chem. 7, (1968), 1818.

134. V.G. Albano, P.L. Bellon, P. Chini, and V. Scatturin, J. Organomet. Chem. 16, (1969), 471.

135. P. Chini, J.C.S. Chem. Comm. (1967), 440.

136. P. Chini and V. Albano, J. Organomet. Chem. 15, (1968), 433.

137a D.W. Hart, R.G. Teller, G. Yuki, R. Bau, G. Longoni, S. Campanella, P. Chini, and T.F. Koetzle, Angew.Chem. Intern. 18 (1978), 80.

137b D.W. Hart, R.G. Teller, C-Yu Wei, R. Bau, G. Longoni, S. Campanella, P. Chini, and T.F. Koetzle, J. Amer. Chem. Soc. 103, (1981), 1458.

138. A.A. Blanchard and M.M. Winsor, J. Amer. Chem. Soc. 56, (1934), 826.

139. W. Hieber and E. Lindner, Chem. Ber. 94, (1961), 1417.

140. M. Pankowski and M. Bigorgne, Compte. Rend. C264, (1967), 1382.

141. W. Hieber and H. Duchatsch, Chem. Ber. 98, (1965), 2530.

142. W. Hieber and U. Teller, Z. Anorg. Allgem. Chem. 249, (1942), 43.

143. F.A. Cotton, A.D. Liehr, and G. Wilkinson, J. Inorg. Nucl. Chem., 1, (1955), 175.

144. S.F.A. Kettle and I. Paul, Adv. Organomet. Chem. 10, (1972), 199.

145. T.L. Brown and D.J. Darensbourg, Inorg. Chem. 6, (1967), 971.

146. Infra Red Spectra of Inorganic & Coordination Compounds, K. Nakomoto, J. Wiley & Sons, (1963).

147. Metal Carbonyl Spectra, P.S. Braterman, Acad. Press, New York, N.Y., (1975).

148. Organotransition Metal Chemistry, R.F. Heck, Acad. Press, N.Y., (1974).

149. D. Seyferth and R.J. Spohn, J. Amer. Chem. Soc. 91, (1969), 4313.

150. W. Beck and R.E. Nitzschmann, Chem. Ber. 97, (1964), 2098.

151. I. Wender, H.W. Sternberg, and M. Orchin, J. Amer. Chem. Soc. 74 (1952), 1216.

152. H.W. Sternberg, I. Wender and M. Orchin, Anal. Chem. 24, (1952), 174.

153. I. Wender, H.W. Sternberg and M. Orchin, J. Amer. Chem. Soc. 75, (1953), 3041.

154. R.B. King, Adv. Organomet. Chem. 2, (1964), 157.

155. J.E. Ellis, J. Organomet. Chem. 86, (1975), 1.

156. W. Hieber, O. Vohler and G. Braun, Z. Naturforsch. 13b, (1958), 192.

157. S.V. Dighe and M. Orchin, Inorg. Chem. 1, (1962), 965.

158. R.B. King, Inorg. Chem. 2, (1963), 531.

159. R.B. King, J. Inorg. Nucl. Chem. 25, (1963), 1296.

160. W.R. McClellan, J. Amer. Chem. Soc. 83, (1960), 1598.

161. K. Inkrott, R. Goetce, and S.G. Shore, J. Organomet. Chem. 154, (1978), 337.

162. C.S. Ilenda, N.E. Shore, and R.G. Bergman, J. Amer. Chem. Soc. 98, (1976), 225.

163. J.E. Ellis and E.A. Flom, J. Organomet. Chem. 99, (1975), 263.

164. C. Ungurenasu and M. Palie, J.C.S. Chem. Comm. (1975), 388.

165. J.A. Gladysz, G.M. Williams, W. Tam, D.L. Johnson, D.W. Parker, and J.C. Selover, Inorg. Chem. 18, (1979), 553.

166. J.M. Burlitch and T.W. Theysen, J.C.S. Dalton (1974), 828.

167. D.L. Reger, D.J. Fauth, and M.D. Dukes, Synth. React. Inorg. Met. - Org. Chem. 7, (1977), 151.

168. J.J. Brunet, C. Sidot, and P. Caubere, J. Organomet. Chem. 204, (1980), 229.

169. I. Rhee, M. Ryang, and S. Tsutsumi, Bull. Chem. Soc. Jpn. 44, (1971), 2552.

170. F. Calderazzo, G. Fachinetti, and F. Marchetti, J.C.S. Chem. Comm. (1981), 181.

171. R.J. Klingler, K. Mochida, and J.K. Koch, J. Amer. Chem. Soc. 101, (1979), 6626.

172. N.L. Holy, N.C. Baenziger, and R.M. Flynn, Angew. Chem. Intern. Edn. 17, (1978), 686.

173. A.B.P. Lever, G.A. Ozin, A.J.L. Hanlan, W.J. Power, and H.B. Gray, Inorg. Chem. 18, (1979), 2088.

174. P.C. Steinhardt, W.L. Gladfelter, A.D. Harley, J.R. Fox, and G.L. Geoffroy, Inorg. Chem. 19, (1980), 332.

175. I. Rhee, M. Ryang, S. Mura, and N. Sonoda, Chem. Lett. (1978), 909.

176. F. Ungváry and L. Markó, J. Organomet. Chem. 193, (1980), 379.

177. L. Cassar and M. Foà, J. Organomet. Chem. 134, (1977), C15.

178. H. Alper, J.K. Currie, and H. des Abbayes, J.C.S. Chem. Comm. (1978), 311.

179. R.F. Heck, J. Amer. Chem. Soc. 86, (1964), 2819.

180. H. Des Abbayes and A.B. Buloup, J.C.S. Chem. Comm. (1978), 1090.

181. R.F. Heck, J. Amer. Chem. Soc. 85, (1963), 3383.

182. P.S. Braterman, B.S. Walker, and T.H. Robertson, J.C.S. Chem. Comm. (1977), 651.

183. R.D. Adams, D.F. Chodosh, N.M. Golembeski, and E.C. Weissman, J. Organomet. Chem. 172, (1979), 251.

184. F. Ungváry, A. Sisak, and L. Markó, J. Organomet. Chem. 188, (1980), 373.

185a B.K. Nicholson, B.H. Robertson and J. Simpson, J. Organomet. Chem. 66, (1974), 53.

185b B.K. Nicholson, and J. Simpson, J. Organomet. Chem. 155, (1978), 237.

186. R.B. King, Acc. Chem. Res. 3, (1970), 417.

187. F.S. Wong and K.M. Mackay, J. Chem. Res. (S) (1980), 109.

188. D.J. Patmore and W.A.G. Graham, Inorg. Chem. 5, (1966), 1586.

189. D.P. Schussler, W.R. Robinson, and W.F. Edgell, Inorg. Chem. 13, (1974), 153.

190. C. Schramin and J.I. Zink, J. Amer. Chem. Soc. 101, (1979), 4554.

191. J.E. Ellis, P.T. Barger, and M.L. Winzenburg, J.C.S. Chem. Comm. (1977), 686.

192. W.D. Closson, P. Wriede, and S. Bank, J. Amer. Chem. Soc. 88, (1976), 1581.

193. G.B. McVicker, Inorg. Synth. 16, (1976), 56.

194. G.B. McVicker and R.S. Matyas, J.C.S. Chem. Comm. (1972), 972.

195. G. Schmid and G. Etzradt, J. Organomet. Chem. 131, (1977), 477.

196. J.P. Barbier and P. Braunstein, J. Chem. Res. (S) (1978), 412.

197. J.W.A. Van der Velden, J.J. Bour, B.F. Otterloo, W.P. Bosman and J.H. Noordik, J.C.S. Chem. Comm. (1981), 583.

198. G.W. Parshall, U.S. Patent 3, 330, 629 (1967); Chem. Abs. 67, (1967), 92434d.

199. J.E. Ellis, J. Organomet. Chem. 111, (1976), 331.

200. A. Moro, M. Foà, and L. Cassar, J. Organomet. Chem. 185, (1980), 79.

201. S. Gamborotta and H. Alper, J. Organomet. Chem. 194, (1980), C19.

202a H. Des Abbayes and A. Buloup, J. Organomet. Chem. 198, (1980), C36.

202b H. Des Abbayes and A. Buloup, Tetrahedron Nett. 21, (1980), 4343.

203. D.H. Gibson, F.U. Ahmed and K.R. Phillips, J. Organomet. Chem. 206, (1981) C17.

204. H. Alper, Adv. Organomet. Chem. 19, (1981), 183.

205. W.F. Edgell, M.T. Yang, and N. Koizumi, J. Amer. Chem. Soc. 87, (1965), 2563.

206. W.C. Price, W.F. Sherman, and G.R. Wikinson, Proc. Roy. Soc. (London) A255, (1960), 1.

207. W.F. Edgell, J. Huff, J. Thomas, H. Lehman, C. Angell, and G. Asato, J. Amer. Chem. Soc. 82, (1960), 1254.

208. W.F. Edgell, J. Lyford IV, A. Barbetta, and C.I. Jose, J. Amer. Chem. Soc. 93, (1971), 6403.

209a W.F. Edgell and J. Lyford IV, J. Amer. Chem. Soc. 93, (1971), 6407.

209b Ion and Ion Pairs in Organic Reactions Vol. 1, M. Szwarc Ed., John Wiley & Sons, (1972), Ch 4, 153.

210. B.W. Maxey and A.I. Popov, J. Amer. Chem. Soc. 89, (1967), 2230.

211. W.F. Edgell and J. Lyford IV, J. Chem. Phy. 52, (1970), 4329.

212. W.F. Edgell and A. Barbetta, J. Amer. Chem. Soc. 96, (1974), 415.

213. W.F. Edgell, S. Hedge and A. Barbetta, J. Amer. Chem. Soc. 100, (1978), 1406.

214. W.F. Edgell and S. Chanjamsri, J. Amer. Chem. Soc. 102, (1980), 147.

215. C.D. Pribula and T.L. Brown, J. Organomet. Chem. 71, (1974), 415.

216. M.Y. Darensbourg, D.J. Darensbourg, D. Burns and D.A. Drew, J. Amer. Chem. Soc. 98, (1976), 3127.

217. A.R. Rossi and R. Hoffman, Inorg. Chem. 14, (1965), 365.

218. V. Gutman, Monatsh. Chem. 108, (1977), 492.

219. U. Mayer, V. Gutman and L. Gerger, Monatsh. Chem. 106, (1975), 1235.

220. W.F. Edgell, A. Watts, J. Lyford IV, and W. Risen Jnr., J. Amer. Chem. Soc. 88, (1966), 1815.

221. W.F. Edgell, J. Lyford IV, R. Wright, W. Risen Jnr., and A. Watts, J. Amer. Chem. Soc. 92, (1970), 2240.

222. B.G. Cox and W.E. Waghorse, Chem. Soc. Rev. 9, (1980), 381.

223a G. Fachinetti, C. Floriani, P.F. Zanazzi, Inorg. Chem. 17, (1978), 3002.

223b H.B. Chini and R. Bau, J. Amer. Chem. Soc. 98, (1976), 2434.

224. H.N. Adams, G. Fachinetti, and J. Strahle, Angew. Chem. Intern. Edn. 19, (1980), 404.

225. B.S. Walker, Ph.D. Thesis, University of Glasgow 1978.

226. G. Bor, Inorg. Chim. Acta 1, (1967), 81.

227. E. Beckmann and T. Paul, Ann. Chem. 226, (1891), 1.

228. J.M. Burlitch, J. Amer. Chem. Soc. 91, (1969), 4563.

229a F.P. Dwyer and E.C. Gyarfas, J. Proc. Roy. Soc. (N.S. Wales) 83, (1949), 263.

229b M.J. Baillie, Ph.D. Thesis, University of Glasgow 1965.

229c D.W.A. Sharp, Adv. Fluorine Chem. 1, (1960), 68.

230. G. Bor and L. Markó, Chem. and Ind. (1963), 912.

231. M. Nitay and M. Rosenblum, J. Organomet. Chem. 136, (1977), C23.

232. Reactions of Coordinated Ligands, P.S. Braterman et. al., Plenum, London and New York, in preparation.

233. Y. Sawa, M. Ryang, and S. Tsutsumi, J. Org. Chem. 35, (1970), 4183.

234. S.A. Fieldhouse, B.H. Freeland, C.D.M. Mann and R.J. O'Brien, J.C.S. Chem. Comm. (1970), 181.

235. R. Colton and M.J. McCormick, Coord. Chem. Rev. 31, (1980), 1.

236. D. Seyferth, Adv. Organomet. Chem. 14, (1976), 97.

237. G. Fachinetti, J.C.S. Chem. Comm. (1979), 396.

238. G. Fachinetti, J.C.S. Chem. Comm. (1979), 397.

239. D. Seyferth, J.E. Hallgren, and P.L.K. Hung, J. Organomet. Chem. 50, (1973), 265.

240. H.A. Hodali, D.F. Shriver, and C.A. Ammlung, J. Amer. Chem. Soc. 100, (1978), 5239.

241. G. Fachinetti, S. Pucci, P.F. Zanazzi, and U. Methong, Angew. Chem. Intern. Edn. 18, (1979), 619.

242. G. Fachinetti, L. Bulocchi, F. Secco, and M. Venturini, Angew. Chem. Intern. Edn. 20, (1981), 204.

243. W.C. Trogler, J. Amer. Chem. Soc. 101, (1979), 6459.

244. H.N. Adams, G. Fachinetti, and J. Strahle, Angew. Chem. Intern. Edn. 20 (1981), 125.

245. C.D.M. Mann, A.J. Cleland, S.A. Fieldhouse, B.H. Freeland, and R.J. O'Brien, J. Organomet. Chem. 24, (1970), C61.

246a N.J. Nelson, N.E. Khim, and D.F. Shriver, J. Amer. Chem. Soc. 91, (1969), 5173.

246b J.C. Kotz and C.D. Turnipseed, J.C.S. Chem. Comm. (1970), 41.

247. G. Schmid, Angew. Chem. Intern Edn. 17, (1978), 392.

248. G. Schmid, K. Bartl, Z. Naturforsch B, Anorg. Chem. Org. Chem. 32B, (1977), 1277.

249. H.A. Hodali and D.F. Shriver, Inorg. Chem. 18, (1979), 1236.

250. D.F. Shriver, D. Lehman and D. Strope, J. Amer. Chem. Soc. 97, (1975), 1594.

251. L.F. Dahl and J.F. Blount, Inorg. Chem. 4, (1965), 1373.

252. H. Beurich, T. Madach, F. Richter, and H. Vahrenkamp, Angew. Chem. Intern. Edn. 18, (1979), 690.

253. G. Longoni, Intern. Conf. on Chem. of Pt. Group Metals, Bristol, (1981), Abstract No. F1.

254. W.F. Edgell and J. Lyford IV, Inorg. Chem. 9, (1970), 1932.

255. W. Hieber, W. Abeck, and J. Sedlmeier, Angew. Chem. 64, (1952), 480.

256. P. Leung, P. Loppens, R. McMullan, and T.F. Koetzle, Acta Cryst. B37, (1981), 1347.

257. G.B. McVicker, Inorg. Chem. 14, (1975), 2087.

258. J.P. Fawcett, A. Pöe, and K.R. Sharmo, J. Amer. Chem. Soc. 98, (1976), 1401.

259. J.P. Fawcett and A. Pöe, J.C.S. Dalton (1977), 1302.

260. W. Hieber, E.O. Fischer, and E. Böckly, Z. Anorg. Allgem. Chem. 269, (1952), 308.

* 262. R.J. Clark, S.E. Whiddon, and R.E. Serfass, J. Organomet. Chem. 11, (1968), 637.

263a G.M. Sheldrick and R.N.F. Simpson, J.C.S. Chem. Comm. (1967), 1015.

263b G.M. Sheldrick and R.N.F. Simpson, J.C.S. A. (1968), 1005.

264. L.M. Bower and M.H.B. Stiddard, J. Organomet. Chem. 13, (1968), 235.

265. G. Bor, Inorg. Chim. Acta 3, (1969), 196.

266. D.M. Adams, J.B. Cornell, J.L. Dawes and R.D.W. Kemmitt, Inorg. Nucl. Chem. Lett. 3, (1967), 437.

267. E.A.C. Lucken, K. Noack and D.F. Williams. J.C.S. A (1967), 148.

268. A.R. Manning, J.C.S. A (1968), 1018.

269. A.T.T. Hsieh and G. Wilkinson, J.C.S. Dalton (1973), 867.

270. O. Kahn, J. Henrion and G. Bouquet, Bull. Soc. Chim. Fr. (1967), 3547.

271. W. Hieber and R. Breu, Chem. Ber. 90, (1957), 1259.

272. W. Hieber and W. Hübel, Z. Elektrochem. 57, (1953), 331.

273. R,B. King and A. Efraty, J. Organomet. Chem. 24, (1970), 241.

274. H.L. Condor and W.R. Robinson, Inorg. Chem. 11, (1972), 1527.

* 261. H. Behrens, Z. Naturforsch. 7b, (1952), 321.

275. A. Vizi-Orosz, L. Papp and L. Markó, Inorg. Chim. Acta 3, (1969) 103.

276. J.M. Burlitch, R.B. Petersen, H.L. Condor and W.R. Robertson, J. Amer. Chem. Soc. 92, (1970), 1783.

277. A.J. Cleland, S.A. Fieldhouse, B.H. Freeland, C.D.M. Mann, and R.J. O'Brien, Inorg. Chim. Acta 4, (1970), 479.

278. G.B. Deacon, Rev. Pure Appl. Chem. 13, (1963), 189.

279. D.N. Duffy, K.M. Mackay, and B.K. Nicholson, J.C.S. Dalton (1981), 381.

280. R.F. Gerlach, K.M. Mackay, B.K. Nicholson, and W.T. Robinson J.C.S. Dalton (1981), 80.

281. K.L. Brown and R.K. Hessley, Inorg. Chim. Acta 53, (1981), L115.

282. F. Glocking, V.B. Mahele, and J.J. Sweeney, J.C.S. Dalton (1979), 767.

283. G.L. Geoffroy and R.A. Epstein, Adv. Chem. Ser. 168, (Inorg. Organomet. Photochem.), (1978), 168.

284. F.H. Carré, F.A. Cotton, and B.A. Frenz, Inorg. Chem. 15, (1976), 381.

285. P.M. Lausarot, G.A. Vaglio, and M. Valle, Inorg. Chim. Acta 35, (1979), 227.

286. H. Haas and R.K. Sheline, J. Inorg. Nucl. Chem. 29, (1967), 693.

287. S. Aime, L. Milone, D. Osella, G.E. Hawkes, and E.W. Randall, J. Organomet. Chem. 178, (1979), 171.

*289. G. Longoni, S. Campanella, A. Ceriotti, P. Chini, W.G. Albano, and D. Braga, J.C.S. Dalton, (1980), 1816.

290. Ibid., 1820.

291. R.C. Ryan, C.U. Pittman Jnr., J.P. O'Connor, and L.F. Dahl, J. Organomet. Chem. 193, (1980), 247.

292. G. Bor, U.K. Dietler, P. Pino, and A. Poe, J. Organomet. Chem. 154, (1978), 301.

*288. M.C. MANNING AND W.A. TROGLER, INORG. CHIM. ACTA 50 (1981) 247.

293. G. Bor and U.K. Dietler, J. Organomet. Chem. 191, (1980), 295.

294. M.F. Mirbach, A. Saus, A.M. Krings, and M.J. Mirbach, J. Organomet. Chem. 205, (1981), 229.

295. D.J. Darensbourg and M.J. Incorvia, J. Organomet. Chem. 171, (1979), 89.

296. D.J. Darensbourg and M.J. Incorvia, Inorg. Chem. 19, (1980), 2585.

297. A.M. Lennertz, J. Laege, M.J. Mirbach, and A. Saus, J. Organomet. Chem. 171, (1979), 203.

298. J.S. Kristoff and D.F. Shriver, Inorg. Chem. 13, (1974), 499.

299. D.S. Shriver, personal communication.

300. F. Ducelliez and A. Raynaud, Bull. Soc. Chim. 15, (1914), 599.

301. T.J. Wydeven and N.W. Gregory, J. Phy. Chem. 68, (1964), 3249.

302. W.C. Nieuwpoort, G.A. Wesselink, and E.H.A.M. Van der Wee, Recl. Trav. Chim. Pays - Bas 85, (1966), 397.

303. J. Ferguson, Prog. Inorg. Chem. 12, (1970), 159.

304. S. Buffagni and T.M. Dunn, Nature 188, (1960), 937.

305. G.W.A. Fowles, D.A. Rice, and R.A. Walton, J.C.S. A (1968), 1842.

306. F.A. Devillanova and G. Verani, Inorg. Chim. Acta 30, (1978), 209.

307. W.L. Driessen and M. den Heijer, Inorg. Chim. Acta 33 (1979), 261.

308. E.M. Boge, D.P. Freyberg, E. Kokot, G.M. Mockler, and E. Sinn, Inorg. Chem. 16, (1977), 1655.

309a P. Dapporto, G. Fallani, and L. Sacconi, J. Coord. Chem. 1, (1971), 269.

309b A. Belanger and P. Brassard, J.C.S. Chem. Comm. (1972), 862.

310. G.R. Newkome, D.K. Kohli, and F. Fronczek, J.C.S. Chem. Comm. (1980), 9.

311a P.S. Braterman, A.E. Leslie, and B.S. Walker, J.C.S. Dalton (1980), 2318.

311b G.R. Newkome, D.K. Kohli, and F. Fronczek, J.C.S. Dalton (1980), 2318.

312. W.L. Driessen, personal communication.

313. S.F. Mason, Structure and Bonding 39, (1980), 43.

314. J. Chatt, J.R. Dilworth, G.J. Leigh and R.L. Richards, J.C.S. Chem. Comm. (1970), 955.

315. F.A. Cotton, D.M.L. Goodgame, and M. Goodgame, J. Amer. Chem. Soc. 83, (1961), 4161 and 4690.

316. F. Basolo, Inorg. Chim. Acta 50, (1981), 65.

317. W.A. Herrmann, H. Biersack, M.L. Sieglar, K. Weidenhammer, R. Siegel, and D. Rehder, J. Amer. Chem. Soc. 103, (1981), 1692.